Aalto University
School of Chemical
Technology

School of Chemical Technology
Degree Programme of Bioproduct technology

Sherif Elsayed

γ-valerolactone fractionation of pine wood

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 21 July, 2016.

Supervisor **Professor Herbert Sixta**

Instructor **PhD Marc Borrega**

Author Sherif Elsayed

Title of thesis γ-valerolactone fractionation of pine wood

Department Forest Products Technology

Professorship Biorefineries **Code of professorship** KM3001

Thesis supervisor Professor Herbert Sixta

Thesis advisor(s) / Thesis examiner(s) PhD Marc Borrega

Date 11-07-2016 **Number of pages** 50+8 **Language** English

Abstract

Fractionation of milled pine wood using γ-valerolactone (GVL)/ water solution as a novel organosolv treatment is proposed. Milled pine wood of 0.125 mm was cooked with GVL/water solution of different ratios. The reaction took place at 180 °C for 120 min in a monowave reactor. It was found that the highest delignification in pulp was achieved over the range of 50% to 60% wt. GVL/water. Under these conditions, the lignin content in the pulp was 12.7% and 14.4% O.D. wood basis, and the pulp yield was 60% and 65% respectively. Additionally, delignification increased when a different batch of samples at 50% and 60% wt. GVL were tested at 200 °C for 120 min. The residual lignin was the lowest at 60% wt. GVL with only 5.9% remaining. There was no significant change in delignification observed when the reaction time was increased to 150 min for the 50% and 60% wt. GVL samples at 180 °C. On the other hand, minor losses in cellulose content were detected at the first reaction conditions. The losses in the cellulose content slightly increased when temperature was raised to 200 °C. On the contrary, hemicelluloses content in pulp, xylan and glucomannan, were readily hydrolyzed. The hydrolysis of hemicelluloses was greatly affected by the increase in temperature, the final hemicelluloses content in pulp at 200 °C was 2.6% O.D. wood at 60% wt. GVL.

For the aim of studying the trend behavior of delignification and polysaccharides hydrolysis, the fractionation reactions were carried out at 180 °C, 195°C and 210°C. As expected, delignification was maximum at 210 °C with only 45 min reaction time, while the least delignification was achieved at 180 °C and 180 min. The same trend is adopted by the hydrolysis of the polysaccharides, where intensive hydrolysis of hemicelluloses was noticed at 210 °C compared to 180 °C. On the contrary, cellulose losses were minor and residual cellulose values were not significantly affected by the increase in temperature.

Finally, the rate constants (K) for delignification and polysaccharides hydrolysis were determined at the reaction temperatures of 180 °C, 195°C and 210°C. The K values showed faster delignification reactions at 210°C with 0.0378 1/min to 0.0225 at 195 °C, while the slowest delignification rate constant was 0.0038 1/min at 180 °C. The activation energy (E) for the delignification reactions was found to be 140.1 KJ/mol. As for polysaccharides, 'semi-crystalline' cellulose hydrolysis was much slower compared to 'amorphous' hemicelluloses hydrolysis at any given temperature, and xylan hydrolysis was faster than that of glucomannan.

Keywords Organosolv; GVL; pine wood; fractionation; delignification; hydrolysis; kinetics

Acknowledgements

My sincere gratitude goes firstly to Professor Herbet Sixta, for accepting me in his research group and giving me the support to develop this work. I would also like to extend my gratitude to PhD Marc Borrega for his continuous support and valuable feedback.

Very special thanks to Quang Le Huy for his endless guidance through the practical lab work. He provided uninterrupted support, comments and feedback whenever required. I would also like to thank Rita Hatakka for her experience in analyzing my many samples, and Yibo Ma for his nice company in the office.

Finally, all my gratitude for my family and Anna, for their support and faith in my endeavors.

Espoo, 10.06.2016

Sherif Elsayed.

Contents

1. Introduction

Since the discovery of conventional fossil fuel in the modern history, our world relies heavily on it. The non-renewable resources are being consumed to improve the quality of people's lives and drive global economy forward. However, continuous depletion of the fossil-based resources along with the environmental deterioration drives the current societies to seek renewable and clean resources for the sustainable supply of fuels and chemicals (Morais, Bogel-Lukasik 2013). The transition to non-conventional fuels is not only driven by political and economic reasons, but more importantly by the environmental concerns associated with petroleum-derived feed stocks. In this context, lignocellulosic biomass, as an alternative, is the most abundant renewable biomass resource and the only current renewable resource on the Earth that can be converted to liquid fuels and chemicals on a mass scale production (Hamelinck, Van Hooijdonk et al. 2005, Chundawat, Beckham et al. 2011). In addition to its sustainability, the use of lignocellulosic biomass as a fuel feedstock is a green process since there is no additional CO_2 emission during the production and utilization of bioenergy, facilitating or even eliminating negative impact on the carbon balance of our nature (Chundawat, Beckham et al. 2011).

Effective utilization of the lignocellulosic biomass is necessary in order to achieve an increasing contribution in decreasing our reliance on petroleum and the gradual independence from it. Hence, biomass treatments and the fractionation into its principle elements, cellulose, hemicelluloses and lignin is essential. For this purpose, nowadays many methods have been developed for wood fractionation within the biorefinery concept, including acidic, alkaline, organosolv, ionic liquids, hydrothermal pretreatment and so forth (Sixta 2006).

Organosolv treatments are gaining more interest recently. The concept of the treatment is to use an aqueous organic solvent as the treatment medium in which the organic solvent will diffuse faster to the wood bulk mass and provide better solvent properties to the wood organic components (Sannigrahi, Ragauskas 2013). The use of γ-valerolactone (GVL) as an organic solvent in the chemical conversion of cellulose and hemicellulose has been studied recently. The use of the novel solvent showed improvement in the carbohydrates conversion to their equivalent monomer sugars, in addition to better delignification profiles over the use of pure water (Fang, Sixta 2015). Moreover, the role of GVL in the reaction mechanisms extends to increase the selectivity of the desired products. However, the understanding of the full scientific basis for the solvent role in the reaction mechanism is not yet fully discovered (Mellmer, Alonso et al. 2014).

The proposed thesis document reports the fractionation of pine wood with GVL/water as an organosolv treatment. Milled pine wood was treated with GVL/water to test the delignification potential of this process at different GVL/water ratios to achieve maximum delignification. In

addition, the effect of increasing the temperature on the yields of the products and the reaction behavior was studied. The thesis also covers the kinetics of the involved pine delignification reactions as well as the polysaccharides hydrolysis reactions.

The thesis document is organized to include: First, literature review section discussing wood structure and its principal elements. Also, the literature review contains an overview of the major pulping technologies (Kraft, acid sulfite pulping and organosolv) with focus on the chemistry of delignification in each technology. Finally, the literature review highlights GVL as a chemical and its reported effect on wood fractionation, in addition to reports of recent studies of water, ethanol, acetic acid and GVL as organosolv solvents. The second section of the thesis covers the experimental part of the thesis including the methods and materials of the lab work as well as the results and discussion parts. In the last section, observations and comments for the lab procedure and the conclusions part can be found.

2. Literature review

2.1. Wood structure

Lignocellulosic biomaterials as mentioned before are the most abundant natural polymers existing on the earth (Sjöström 1993a, Fengel, Wegener 1983). In order to fully exploit them in green and renewable applications, the chemical structure and the role of each wood element should be first highlighted. As most lignocellulosic biomass, wood consists of three predominant components making up to 95-97% of its structure. The three principle elements are cellulose, hemicelluloses and lignin (Sjöström 1993a, Fengel, Wegener 1983).

Cellulose, a C6-polysaccharide with high native DP ranging between 5000-15000 (Sjöström 1993c), is the main structural element in the wood. It has a semi-crystalline structure with anhydro-glucose monomers forming the backbone of the chain. The repeating monomer of cellulose is (1,4)-β-D-glucopyranose (Sjöström 1993c). Around 40% of softwood and 40-50% of hardwood consist of cellulose. The rigid structure of cellulose reinforces wood and plants with the sufficient strength to endure in the nature (Sjöström 1993c, Clair, Alméras et al. 2006). For this reason, cellulose is insoluble and resistant to chemical reactions. When extracted, cellulose fibers have numerous applications, for instance, paper and packaging industries, films, renewable plastic co-polymers, cosmetics, food additives, cellulose-based hydrogels and thickening agents (Kamide 2005). Hemicelluloses too, are polysaccharides with low DP of less than 200 (Sjöström 1993b). Unlike cellulose, hemicelluloses have amorphous structure that can easily be hydrolyzed in elevated temperatures. Typically, they comprise 23-30% of softwood and up to 40% of hardwood. Xylan (C5) is one type of hemicelluloses, found more dominantly in hardwoods. In softwoods, both xylan and glucomannan (C6) are present, with bigger proportions of the latter (Sjöström

1993b). Chemical structure of cellulose, xylan and glucomannan are demonstrated below in Fig. 1,2 and 3.

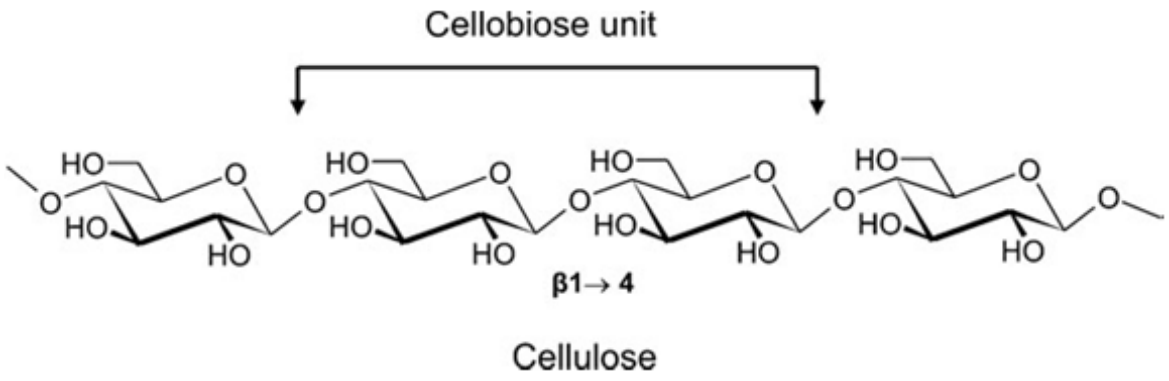


Fig. 1 *(1,4)-β-D-glucopyranose units in cellulose chain (S*jöström *1993c, Clair, Alméras et al. 2006)*

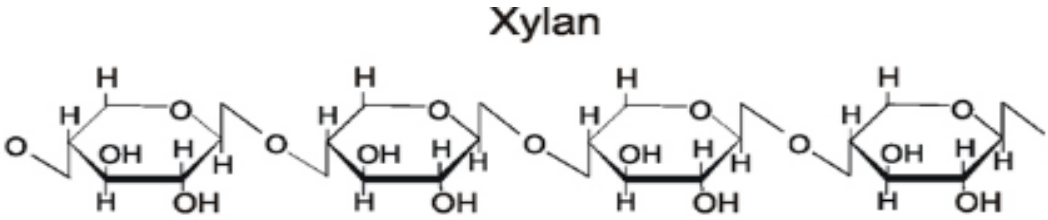


Fig. 2 *Xylan chemical structure (S*jöström *1993c, Clair, Alméras et al. 2006)*

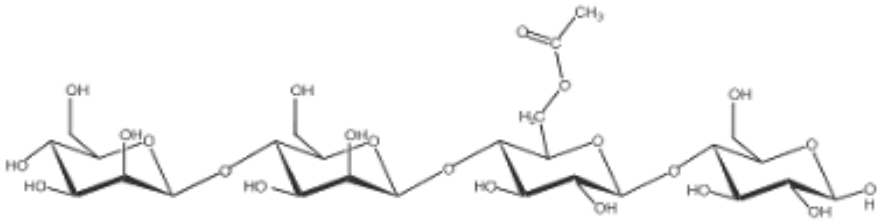


Fig. 3 *Glucomannan chemical structure (S*jöström *1993c, Clair, Alméras et al. 2006)*

On the other side, lignin is a complex and heterogeneous biomacromolecule, as seen in the below Fig. 4, consisting of phenylpropane units with various functional groups. The primary monomers of lignin are guaiacyl, syringyl, and p-hydroxyphenyl, the monomers content depends on the type of the biomass. Lignin can constitute 27-33% of softwood and 23-40% of hardwood (Gordobil, Moriana et al. 2016). The aromatic component plays an essential role in gluing the fibers together,

providing the biomass with the necessary required mechanical strength. In addition to its gluing properties, lignin and hemicellulose play an important role in balancing the water cycle in the lignocellulosic biomass (Sjöström 1993d). The predominant bonds linking lignin molecules together are β-O-4 and α-O-4 linkages, along with less frequent bond types, C-O and C-C linkages (Sjöström 1993d).

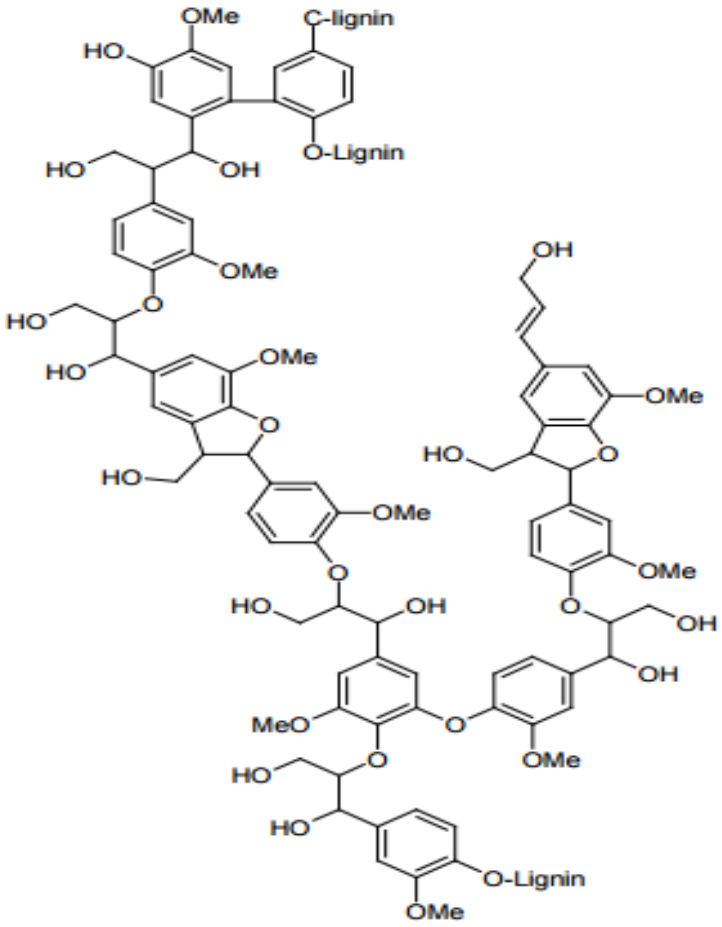


Fig. 4 *Lignin molecule with common linkages (S*jöström *1993d)*

In addition to the three main elements in wood, small fractions of extractives are present (Fengel, Wegener 1983, Hon, Shiraishi 2000). Extractives are organic non-polymer compounds and can be extracted during wood fractionation. Most common extractive types are diterpenoid, monoterpene and fatty acids (Fengel, Wegener 1983, Hon, Shiraishi 2000).

In order to achieve wood fractionation and obtain the principle elements, it is important to overcome the lignin binding properties and separate it in order to isolate the carbohydrates portion. The yield fibers are referred to as pulp and the process is known as delignification of wood. There

are multiple known physical and chemical treatment processes to delignify wood. This thesis focuses and discusses mainly organosolv as a chemical treatment.

Chemically produced pulp is the predominant pulp produced worldwide, accounting for more than 77% of all world fibrous material produced in 2000. The mechanism of chemical treatments for wood fractionation is governed by the pH of the reaction medium. Either alkaline or acidic, the pH, along with the solvent type and properties are the main factors determining the involved fractionation reactions (Blechschmidt, Heinemann 2008). The most common alkaline chemical wood treatment is Kraft wood pulping process. Acidic fractionation, on the other hand, is applied industrially in acid sulfite wood pulping process. In addition to novel –under research- concepts as Ionic liquids and Organosolv solutions (Fengel, Wegener 1983, Sjöström 1993e, Sixta 2006, Blechschmidt, Heinemann 2008).

The goal of the mentioned technologies is not only to delignify wood, but also to produce pulp of good properties. Degree of polymerization, fiber length, fiber strength and bleaching of fibers are important properties for commercial fibers (Blechschmidt, Heinemann 2008).

The next section will briefly overview alkaline kraft treatment and acid sulfite treatment. With focus on delignification mechanism in the two concepts. Moreover, the section will discuss and explain organosolv treatments and the role of organic solvents in wood hydrolysis in the light of recent studies.

2.2. Fractionation treatments

2.2.1. Alkaline, Kraft pulping

Kraft pulping is the largest industrially applied pulping technology. Almost 90% of all chemical pulp produced is from Kraft process (Sixta, Potthast et al. 2008, Sjöström 1993e). The technology is old and the troubleshooting are well-known. In this process, the active ingredients are the hydroxide and the hydrosulfide ions present in the cooking liquor, in the form of NaOH and Na_2S, known as white liquor (Sixta, Potthast et al. 2008, Sjöström 1993e). Delignification is initiated by the reaction of the hydrosulfide ions with lignin, cleaving the β-O-4 and α-O-4 linkages connecting the lignin molecules. Usually, delignification proceeds over three phases, initial, bulk and residual delignification. In the initial phase, the 15-25%, β-O-4 and α-O-4 bonds between the phenolic molecules are cleaved. In addition to delignification, carbohydrate losses due to peeling, hydrolysis and other degradation reactions are observed in this phase (Sixta, Potthast et al. 2008, Sjöström 1993e). On the other hand, in the bulk phase, delignification of only non-phenolic β-O-4 linkages in lignin takes place, as proposed in Fig. 5. Finally, in residual delignification around 15% of the native lignin is removed. It is worth to note that extensive delignification is accompanied by unfavored dissolution in the polysaccharides portion, resulting in loss in pulp yield. For this reason,

delignification is further achieved by other means like oxygen-delignification (Sixta, Potthast et al. 2008, Sjöström 1993e).

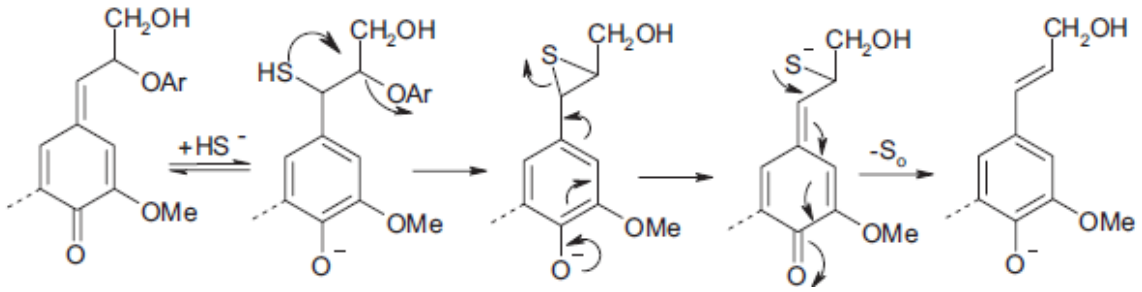


Fig. 5 *Mechanism of delignification in alkaline Kraft treatment (S*jöström *1993e)*

The sustainability of the alkaline process is achieved by the regeneration and recycling of the cooking chemicals. After the reaction, the cooking spent liquor, weak black liquor, is first pumped to evaporators, where the spent liquor is concentrated by evaporation of the existing water. The dry solids content in the liquor increases from 15% to more than 60%. The liquor changes to the commonly known black liquor (Sixta, Potthast et al. 2008). Turpentines are valuable chemicals that can be extracted from the top of the evaporators (Sjöström 1993e). Lignin in the black liquor is then incinerated in the recovery boiler (Sjöström 1993e). The recovery boiler purpose is to generate heat and power enough to make the process energy self-sufficient. During incineration Na_2S is regenerated in the reducing zone in the boiler. As for NaOH, the regeneration is achieved by the aid of slaked lime (CaO) that is produced from heating limestone ($CaCO_3$) in the limekiln (Sixta, Potthast et al. 2008).

2.2.2. Acid sulfite pulping

The origin of the sulfite process dates back to 1867, when calcium hydrogen sulfite and sulfur dioxide were used in treating vegetables to produce paper pulp. Later, in 1874 the first mill using acid sulfite process started production in Bergvik, Sweden. The process uses acidic conditions since calcium sulfite is soluble at pH of less than 2.3. One of the drawbacks to using calcium is the decomposition into calcium sulfate and hydrated SO_2. Thus, high dosages of SO_2 needed to be charged to avoid the deposition of calcium sulfate. Another drawback of calcium is formation of calcium sulfate during recovery process. Calcium sulfate require temperatures of 1200 °C to achieve its decomposition to CaO and SO_2, which is essential in the sulfite reactions mechanisms. To overcome these drawbacks, today, almost all dominating sulfite pulping processes have adopted magnesium instead of calcium. The corresponding pH at which magnesium sulfite is soluble is even higher at 5-6 (Gierer 1986, Sixta, Potthast et al. 2008).

In acidic conditions and with the presence of SO_2 lignin reactions are highly dependent on the pH of the reaction medium. Lignin main degrading reactions in acid sulfite pulping are hydrolysis and sulfonation along with some extent of sulfitolysis (Gierer 1986). Also, in acidic conditions, condensation of lignin can take place as a counter delignification step. The β-O-4 bond show resistance to degradation at low pH values (Gierer 1986). Hence, no cleavage in the lignin macromolecule takes place. Cleavage is only observed in the α-substituents in the lignin chain as seen in Fig. 6.

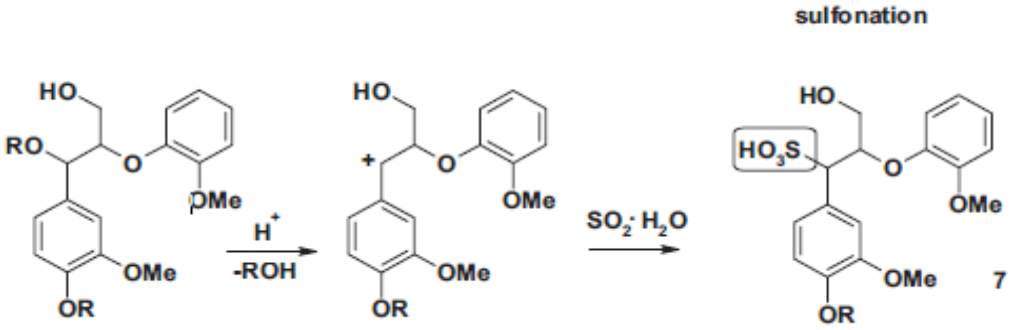


Fig. 6 *Sulfonation of α-substituents in a β-O-4 lignin bond (Tanbda, Nakano et al. 1987)*

The β-O-4 bond ether bond is less stable at relatively higher pH conditions. Thus, with increasing the pH of the acid sulfite pulping, the strong nucleophiles (sulfite and bisulfite) are able to breakdown the ether bond in a sulfitolytic cleavage, converting the lignin into styrene-α-sulfonic acids (Luthe 1990), Fig. 7.

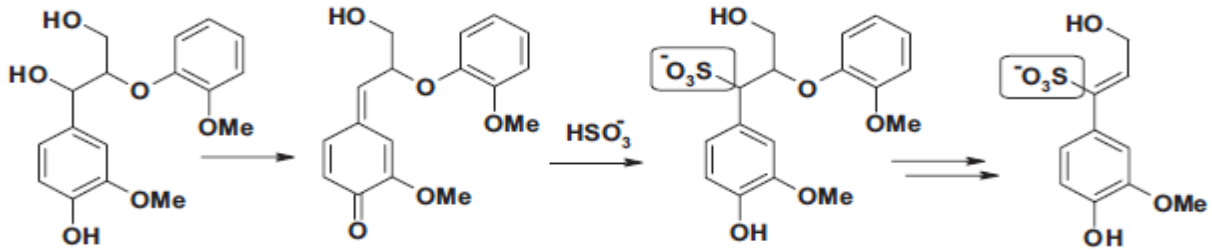


Fig. 7 *Reactions of β-O-4 ether bond in neutral sulfite pulping (Luthe 1990)*

Polysaccharides undergo hydrolysis reactions, resulting in the cleavage of the glycosidic bond in the cellulose and hemicelluloses backbone chain (Gierer 1986). Also, dehydration reactions of C-6 and C-5 take place yielding furfural and HMF as shown in the organosolv section. In addition to dehydration, other side reactions can take place. Part of the hydrogen sulfite is consumed by the reducing end group in the sugar monomers forming α-hydroxysulfonates and subsequent oxidation to aldonic acids, shown in Fig. 8. The oxidation side reactions reduce the sulfite concentration in the cooking liquor. Thus, destabilizes the reaction mechanism (Sixta, Potthast et al. 2008).

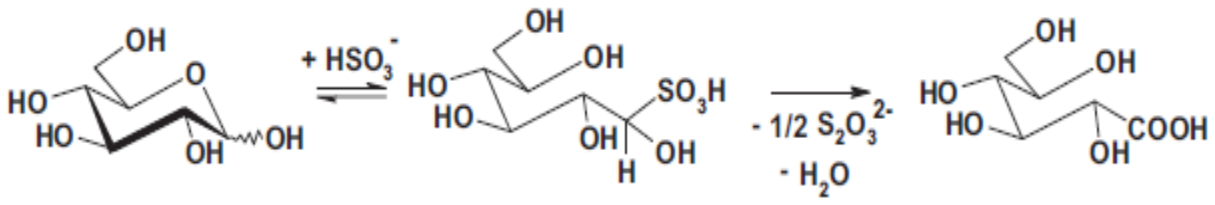


Fig. 8 *Oxidation of monosugars to* α-hydroxysulfonates and subsequent formation of aldonic acids (Sixta, Potthast et al. 2008)

2.2.3. Organosolv

Organosolv treatments for wood were first researched and reported by Kleinert and Tayenthal in 1931 (Johansson, Aaltonen et al. 1987). The organic based solvents were discussed as an alternative cooking method for Kraft and sulfite pulping processes, known for their environmental concerns. Kleinert and Tayenthal proposed using aqueous ethanol in delignification of wood, since faster diffusion of the organic solvent into the wood mass is favored, in addition to better sugars and lignin solubility in the liquor (Muñoz, Mendonça et al. 2007). Comparison of the results from organosolv pulping and the conventional Kraft and sulfite pulping showed more pulp yield in the organosolv at equivalent Kappa number values (Johansson, Aaltonen et al. 1987). Moreover, the strength of the pulp fibers from organosolv pulping is of comparable figures to that of Kraft and sulfite pulps (Muñoz, Mendonça et al. 2007).

Mechanism of organosolv delignification

In acidic conditions, the delignification of wood proceeds through the hydrolysis of lignin-hemicelluloses linkages and internal lignin bonds. The hydrolysis reactions are promoted by acid-catalyzed reactions at elevated temperatures. It is known that the cleavage of the aryl ether linkages in lignin structure is the main responsible factor for the break-down of lignin. From these aryl ether bonds, α-O-4 ether bond is cleaved more easily, whereas β-O-4 requires more drastic acidic conditions in order to be broken. It is agreed that the cleavage of the α-O-4 ether bond is the rate-controlling step in Organosolv treatments. Several pathways were proposed to explain the delignification mechanism (Mcdonough 1992, Sannigrahi, Ragauskas 2013).

1. Solvolytic splitting of the α-O-4 and β-O-4 linkages via the formation of quinone methide intermediate, observed in Fig. 9. It is believed that the following mechanism takes place when a free phenolic group in the para position is present.

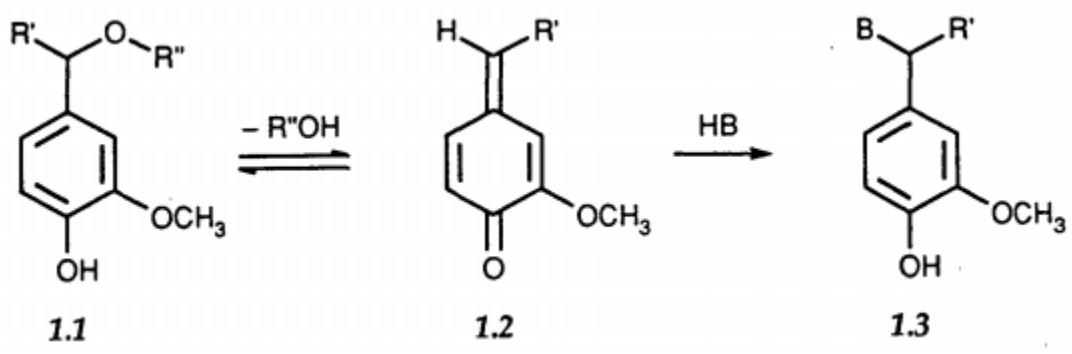


Fig. 9 *Mechanism of solvolytic splitting of lignin with the formation on quinone methide intermediate (Mcdonough 1992). B is OH or OCH3 etc*

2. Direct break-down of the ether bond, with solvolytic splitting by nucleophilic substitution in the benzylic position by an S_N2 mechanism (Fig 10).

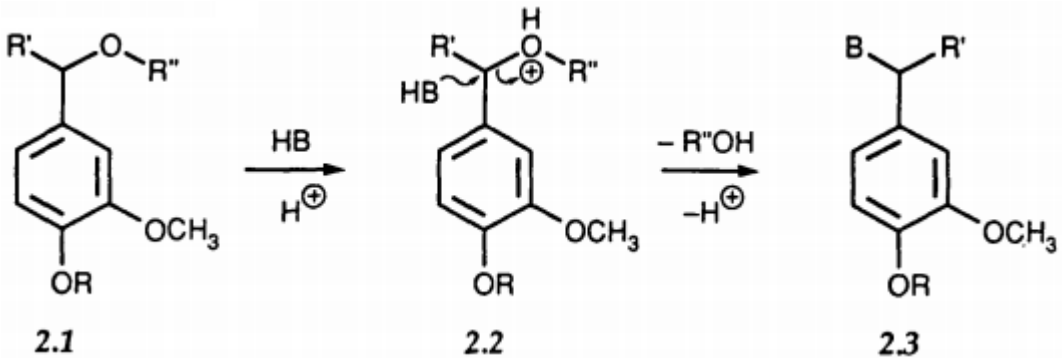


Fig. 10 *SN2 mechanism, nucleophilic substitution in lignin side chain (Mcdonough 1992)*

3. Reaction via formation of benzyl carbocation structure under acidic conditions (Fig.11).

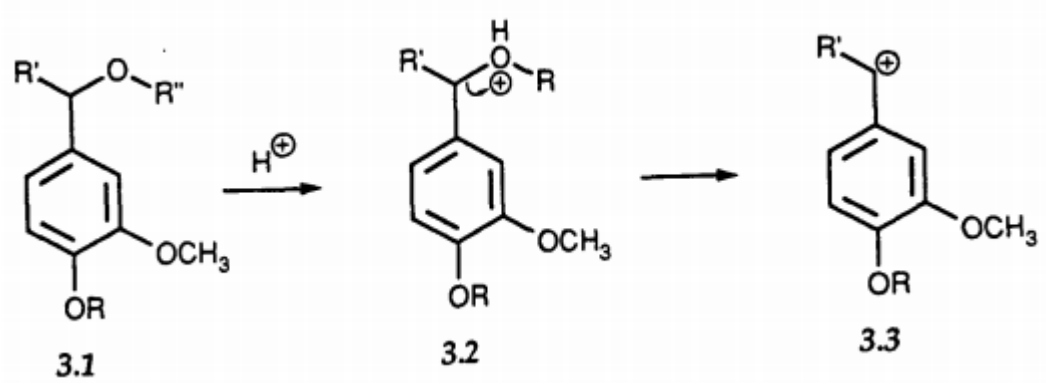


Fig. 11 *Formation of benzyl carbocation structure during delignification (Mcdonough 1992)*

Another reaction type can also occur alongside delignification, where the cleavage of the β-O-4 can form a new bond with another electron-rich carbon atom in a neighboring lignin unit (Fig. 12). These are known as condensation reactions (Mcdonough 1992).

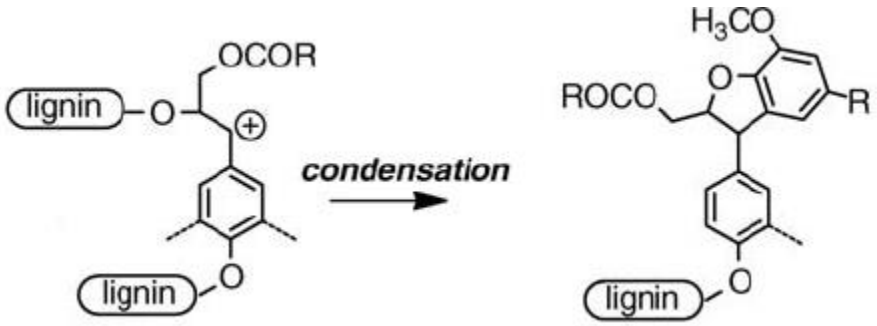


Fig. 12 *Common condensation structure form of lignin (Mcdonough 1992)*

Hydrolysis of carbohydrates, as in acid sulfite pulping, take place mainly in hemicelluloses and less intensively in cellulose, since the glucoronopyranosidic bonds are more stable. The hydrolysis reactions cleave the glycosidic bond connecting the repeating monomer in the backbone, resulting in depolymerization of the chain and producing mono and oligo-saccharides that are soluble in the cooking liquor (Gierer 1986). In addition to hydrolysis, acetyl groups found in hemicelluloses side chains are also cleaved, forming acetic acid. Also, dehydration of C5 and C6 sugars occurs generating furfurals along with further degradation reactions, for instance, hydration of HMF yielding levulinc acid and formic acid. The mechanism of the acid involved hydrolysis and dehydration reactions is illustrated in Fig. 13, 14 and 15.

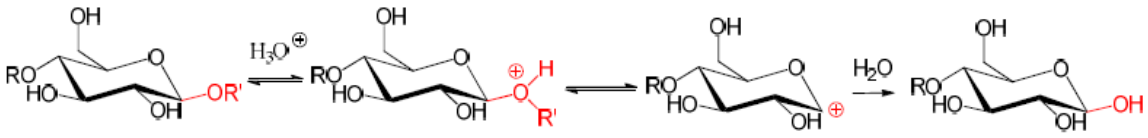
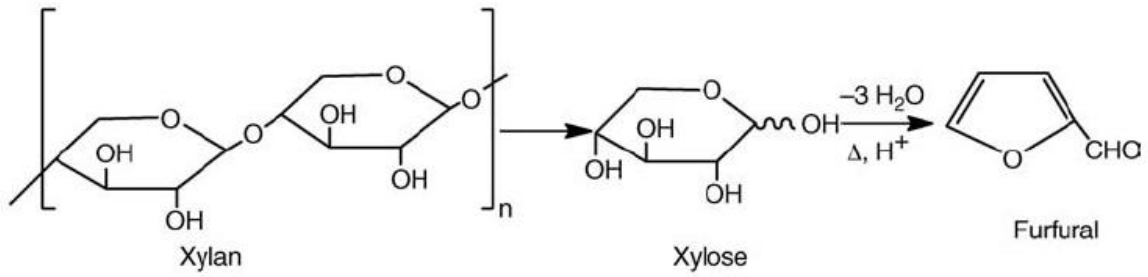


Fig. 13 *Cleavage of glycosidic bond in polysaccharides back bone (Johansson, Aaltonen et al. 1987)*



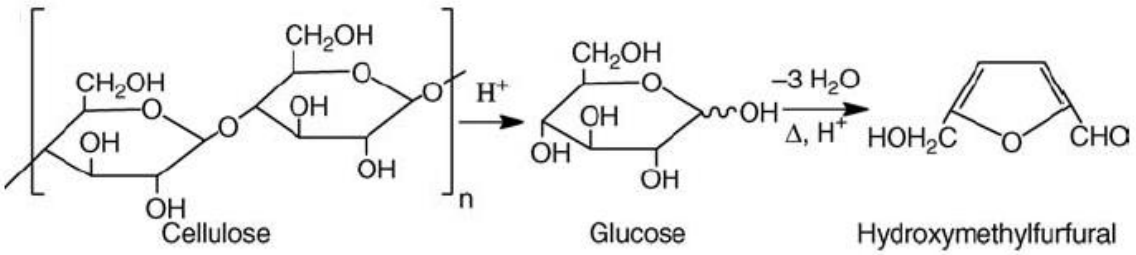


Fig. 14 *Dehydration of sugars and production of furural from xylose and HMF from glucose (Iakovlev, You et al. 2014)*

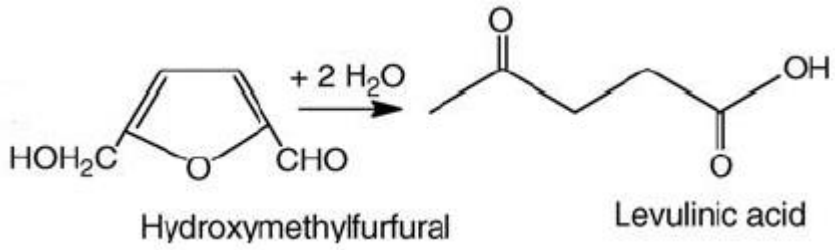


Fig. 15 *Hydration of HMF and the production of levulinic acid (Iakovlev, You et al. 2014)*

Organosolv treatments are frequently used as pretreatment step in the enzymatic hydrolysis of biomass (Sannigrahi, Miller et al. 2010). The use of ethanol/water solvent as pretreatment of loblolly pine in the presence of sulfuric acid as catalyst was found to improve the hydrolysis rate of cellulose to glucose prior to enzymatic treatment. In addition, high delignification was reported with 11.4% residual lignin present from the initial 29.4% (Sannigrahi, Miller et al. 2010), and given that pine wood exhibits difficult delignification (Vázquez, Antorrena et al. 1997).

In another report, acetic acid was used as an organosolv solvent to study the kinetics of delignification of pine wood (Vázquez, Antorrena et al. 1997). It was found that maximum delignification is achieved when 90% concentrated acetic acid was used in the absence of HCl catalyst at 180 °C (left figure), where 90% of the lignin was removed from the initial lignin content 32% O.D. wood basis (Fig. 16). Contrarily, at lower temperatures, higher amount of residual lignin was present with 85% delignification at 160 °C and 40% at 140 °C. On the other hand, when HCl of 0.1% concentration was used (right figure), acceleration in delignification profile was detected with higher delignification values in shorter reaction times. But on the other side, lignin condensation reactions were also present which decreased the soluble lignin fraction.

The delignification constants of the experiment are shown in Table 1 below. The table shows faster delignification constants when HCl was used. The presence of 0.1% HCl was sufficient to increase

the delignification constant k_d value to 6.29 x 10^{-2} min^{-1} from 2.39 x 10^{-3} min^{-1} when no HCl was used.

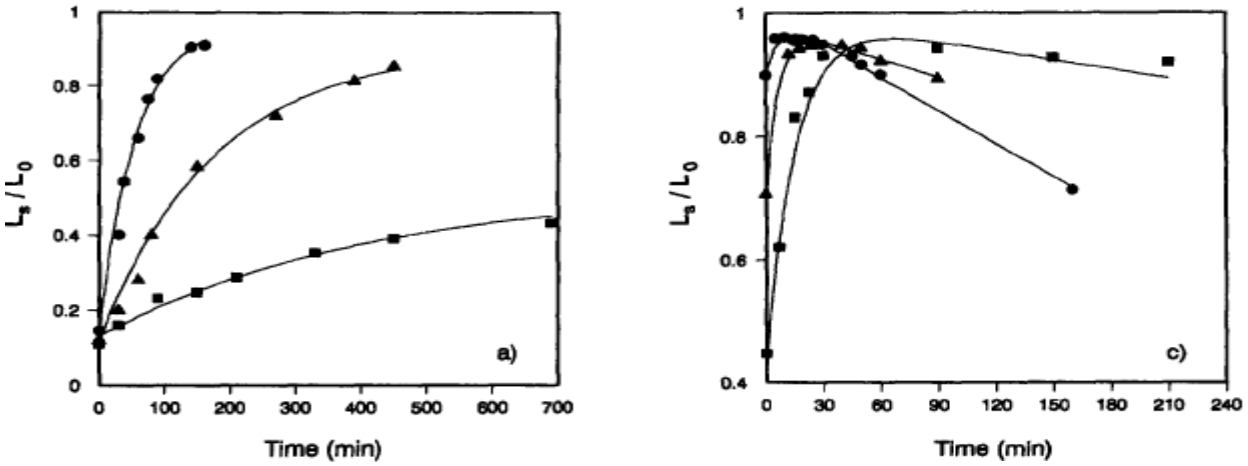


Fig. 16 *Soluble lignin Ls fraction after acetic acid treatment at 140 °C (squares), 160 °C (triangles) and 180 °C (circles), left figure is HCl free and right figure is with 0.1% HCl (Vázquez, Antorrena et al. 1997)*

Table 1 delignification and condensation rate constants as function in temperature and HCL percentage (Vázquez, Antorrena et al. 1997)

T (°C)	[HCl] (%)	k_d $(min)^{-1}$	k_c $(min)^{-1}$
140	0	2.39×10^{-3}	8.93×10^{-7}
160	0	5.64×10^{-3}	0
180	0	1.76×10^{-2}	4.45×10^{-6}
140	0.05	2.76×10^{-2}	2.53×10^{-4}
160	0.05	8.72×10^{-2}	4.67×10^{-4}
180	0.05	1.90×10^{-1}	9.31×10^{-4}
140	0.10	6.29×10^{-2}	5.42×10^{-4}
160	0.10	1.50×10^{-1}	1.06×10^{-3}
180	0.10	—	2.20×10^{-3}

In a similar study, with 95% acetic acid as a solvent for pine wood, the highest delignification achieved was around 72% from the initial 31% O.D. basis with 0.15% HCl at 115 °C (Parajo, Alonso et al. 1995), as observed in Table 2. In this study the condensation reactions are clearer, especially at 130 °C and with 0.45% HCl, where after only 20 minutes of reactions, only 6.8% of lignin is present. The value is then significantly increased due to the continuous C-C bonds formed between lignin and carbohydrate molecules, with total lignin of 41.7% after 3 hours (Parajo, Alonso et al. 1995). The delignification rate constants are shown in Table 3, where faster delignification and condensation reactions are promoted at higher temperatures and in the presence of higher concentration of HCL catalyst.

Table 2 Lignin content and pulp yield at 115 °C and 130 °C at different reaction conditions (Parajo, Alonso et al. 1995)

time (min)	lignin content of solid residues (g/100 g, O.D. basis) 0.15% HCl	0.25% HCl	0.35% HCl	0.45% HCl	pulp yield (g recovered/100 g of initial wood, O.D. basis) 0.15% HCl	0.25% HCl	0.35% HCl	0.45% HCl
(a) Experiments Performed at 115 °C								
0	31.5	31.5	31.5	31.5	100	100	100	100
15	26.5	26.4	25.9	24.3	86.3	81.0	80.0	74.6
30	24.2	22.0	21.7	15.8	75.9	69.4	66.7	55.5
60	20.1	18.1	9.5	8.7	65.7	59.0	47.9	47.5
90	13.4	10.2	10.1	8.4	55.5	50.5	47.0	46.1
120	14.2	11.2	10.1	9.2	53.8	48.4	45.8	44.1
180	9.1	9.3	10.3	12.0	48.5	46.3	44.7	44.2
(b) Experiments Performed at 130 °C								
0	31.5	31.5	31.5	31.5	100	100	100	100
20	20.2	17.4	14.9	6.8	63.5	55.0	52.4	43.3
40	19.0	8.3	7.5	6.1	60.8	46.5	44.1	41.3
60	13.5	13.5	14.3	17.2	51.2	46.3	44.3	45.7
120	10.6	17.8	24.7	33.1	46.2	45.5	48.7	53.0
180	9.53	22.4	33.2	41.7	43.3	48.4	52.4	58.1

Table 3 delignification and condensation rate constants at different reaction conditions (Parajo, Alonso et al. 1995)

temp (°C)	HCl concn (%)	k_1 (min^{-1})	k_2 (min^{-1})
115	0.15	0.0172	0.0010
115	0.25	0.0229	0.0010
115	0.35	0.0284	8.54×10^{-4}
115	0.45	0.0396	8.32×10^{-4}
130	0.15	0.0303	0.0012
130	0.25	0.0639	0.0028
130	0.35	0.0834	0.0045
130	0.45	0.1656	0.0067

2.3. Y-Valerolactone (GVL)

2.3.1.Structure and properties

GVL was firstly suggested by the Hungarian researcher István T. Horváth as a promising green solvent for biomass fractionation (Horváth, Mehdi et al. 2008). GVL is a common type of lactones with the chemical formula $C_5H_8O_2$, Fig. 17. It is a clear colorless liquid with density of 1046 Kg/m^3 similar to the density of water. It has a molecular weight 100.12, boiling point at 208 °C and high flash point of 81 °C. The vapor pressure is only 0.5 mmHg compared to 30 mmHg of water at

normal conditions (Alonso, Wettstein et al. 2013). GVL is stable and shows no degradation in its structure even after months of storage in presence of water and oxygen at room temperature (Horváth, Mehdi et al. 2008).

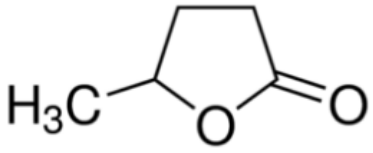


Fig. 17 *GVL chemical structure (Alonso, Wettstein et al. 2013)*

2.3.2. Uses and applications

GVL has wide applications as a food additive, in perfumes, as an intermediate for other organic compounds. Moreover, it is considered a green solvent. It can be produced from the conversion of the biomass derived levulinic acid via hydrogenation. It is soluble in water and shows good properties in biomass valorization (Horvth 2008).

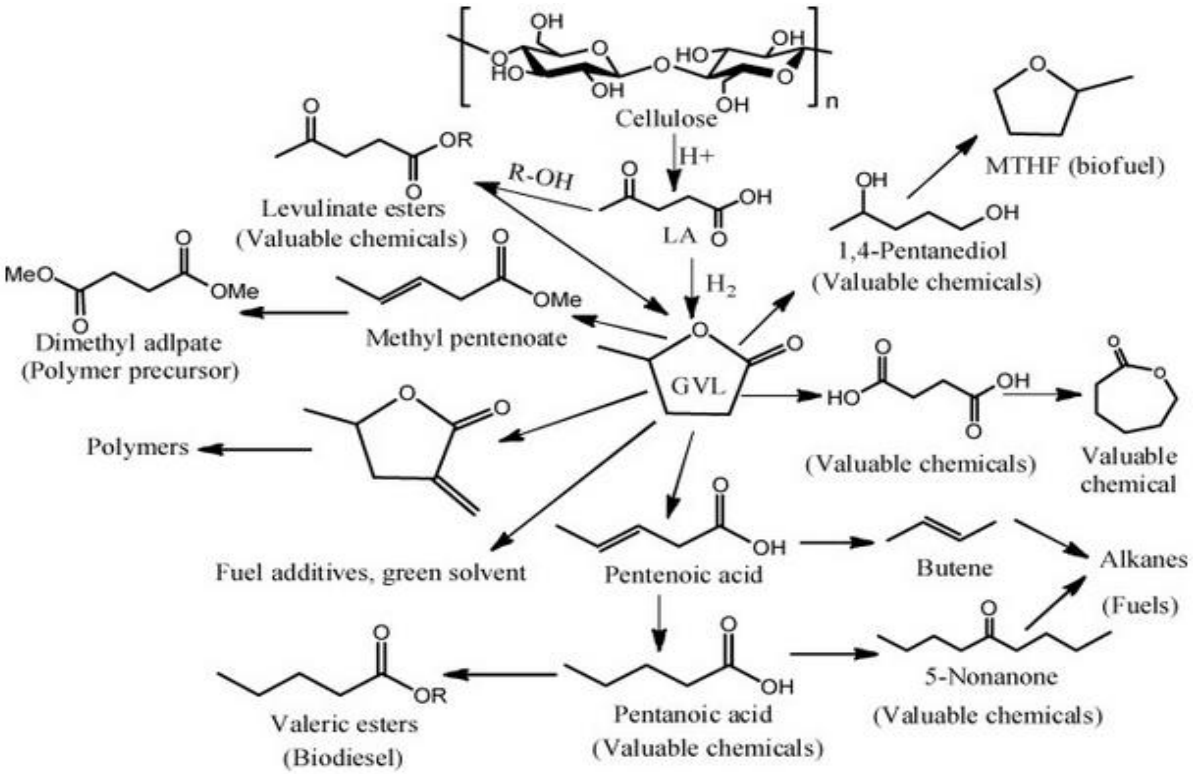


Fig. 18 *Chemicals obtained from upgrading of GVL (Yan, Yang et al. 2015)*

GVL is not only considered as a renewable green solvent, but in addition, it is an important chemical intermediate that can be upgraded to fuels and more value-added chemicals. Catalytic upgrading of GVL can produce, MTHF biofuel, alkanes that can be further upgraded to fuels, biodiesel in the form of valeric esters and polymers and polymer precursor such as levulinate esters, and more. The above Fig. 18 presents the possible chemicals synthesized from GVL (Yan, Yang et al. 2015).

2.3.3. Production of GVL

GVL being viewed as a green solvent can be produced from cellulose and hemicelluloses. During wood cooking, C5 and C6-polysaccharides undergo –at high temperatures- dehydration reactions, resulting in the formation of furfural and HMF respectively. The presence of water in the reaction medium subsequently initiate hydration reactions of furfural to yield LA and HMF to yield LA and FA. LA can then be hydrogenated to GVL through homogeneous or heterogeneous catalytic systems (Fengel, Wegener 1983, Tang, Zeng et al. 2014, Sheldon 2014). A detailed mechanism of the possible conversion reactions of cellulose and xylan to LA then to GVL is illustrated in the below Fig. 19.

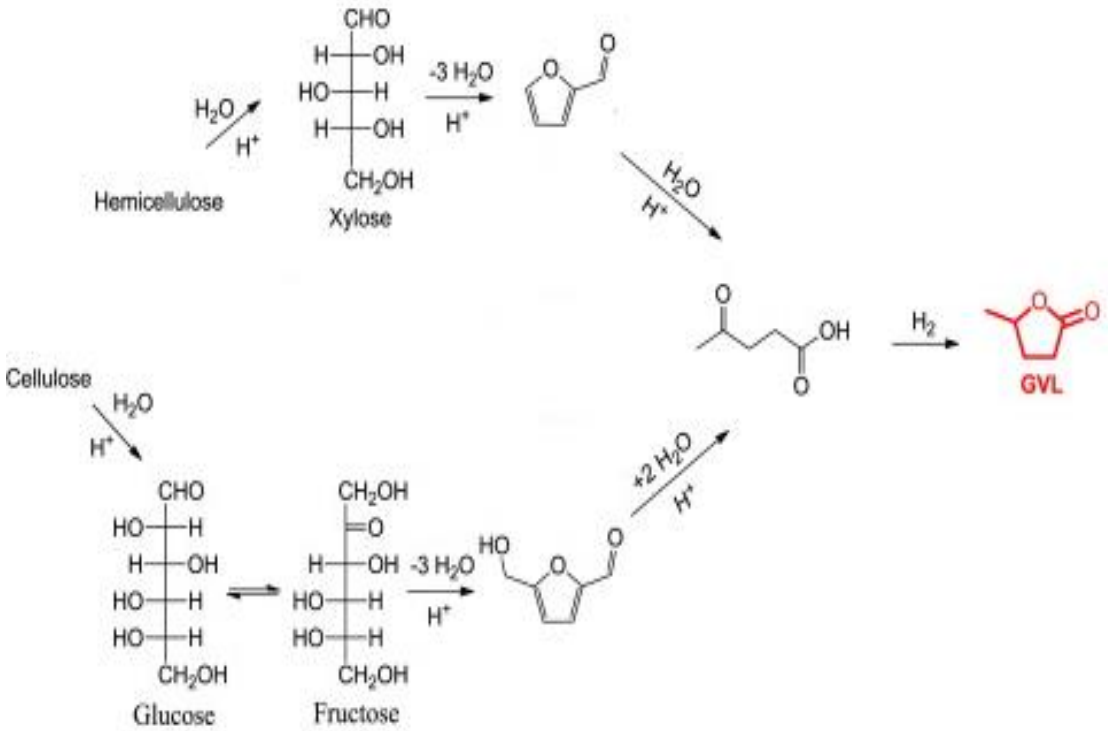


Fig. 19 *GVL production from cellulose and hemicelluloses (Tang, Zeng et al. 2014)*

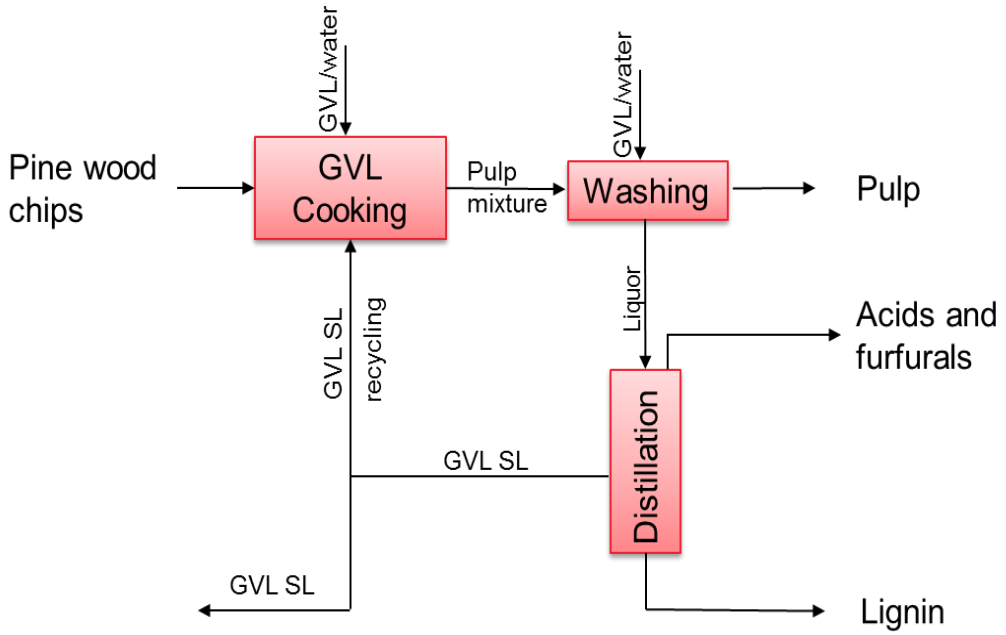
The hydrolysis of cellulose and production of levulinic acid using solid acid catalysts in presence of GVL solvent was studied and reported (MartinAlonso, Marcel R Gallo 2013). The reaction was conducted at 160 °C and using Amberlyst 70 as a catalyst. An increase in the produced LA was observed accompanied by the increase in GVL to water fraction, with 69% LA yield after 16 hours with GVL/water of 9:1 and even higher when GVL/water of 9.5:1 was used. On the contrary, if 100% GVL was used the LA yield dropped significantly to 20% (MartinAlonso, Marcel R Gallo 2013). This indicates that the presence of water in the reaction promotes hydrolysis. The use of GVL/water as a solvent eliminates the need of drying and favors the use of wet feedstocks.

The green solvent can be produced by hydrogenation of LA. In the previous study, after filtration of the produced LA, hydrogenation was initiated over $RuSn_4$/C catalyst at 170 °C. The rate of GVL yield was 0.03 mol min^{-1} g_{cat}^{-1} (MartinAlonso, Marcel R Gallo 2013). Other catalysts were also tested for the same purpose. GVL with yield as high as 99% was obtained when iridium pincer catalyst complex was used instead of $RuSn_4$/C at 100 °C (Li, Xie et al. 2012). Also, platinum oxide, Raney nickel, rhodium and ruthenium complexes are catalysts that can be used for the hydrogenation of LA and production of GVL (Girisuta 2007, Broekhuis, Heeres et al. 2012).

2.3.4. GVL recycling concept

During the recent years, the study of GVL as a green solvent for biomass utilization is gaining continuous interest. GVL has proven to improve the hydrolysis of the wood components and to increase the selectivity of the desired reaction products and lower the activation energy for the desired reactions (Horváth, Mehdi et al. 2008, Mellmer, Alonso et al. 2014, Fang, Sixta 2015).

Moreover, owing to its low vapor pressure, the separation and recycling of GVL from reaction products is assumed to be a simple process. Based on the difference in boiling point between GVL and less volatile acids and furfurals, the latter can be removed by distillation (Horváth, Mehdi et al. 2008). A simple scheme of a future application of GVL in a larger scale can follow Scheme 1 proposed below. Starting with wood pretreatment, the wood chips will then proceed to the digester where continuous GVL is fed. Post cooking, the products mixture is washed with less concentrated GVL/water mixture. After washing, pulp is extracted and can be further bleached and used in relevant applications. Washing filtrate containing spent GVL, acids and furfurals, mono and oligo-sugars, and lignin can be separated in a distillation column. Due to the relatively-higher vapor pressure of acids and furfurals, they are expected to be the most volatile and would be extracted from the top of the distillation column. On the other hand, SL containing GVL with soluble mono and oligo-sugars are less volatile, allowing the stream to exit the column from an intermediate tray. After that, the stream can then be either recycled back to the digester or be further treated to extract the sugars. Finally, dissolved lignin as the heaviest component along with fraction of the SL can be obtained from the bottom.



Scheme 1 Wood fractionation and post separation with GVL solvent

2.3.5. GVL in lignocellulosic fractionation

The study of GVL in the delignification of cotton stalk was studied and reported (Wu, Liu et al. 2016). Different GVL to water ratios were tested, 90:10, 80:20, 70:30 and 60:40, and the reactions took place at 170 °C for 1 hour with L:W ratio of 15:1 and the addition of 10 mM of H_2SO_4. The analyzed lignin yield in SL was determined and was found that 80% GVL corresponded to maximum delignification, with lignin content in SL of 64.7% dry weight. On the other hand, when the water content is further reduced, as in 90% GVL, less delignification was achieved as a result of less hydronium ions present for the breakdown of the lignin structure. The lignin value in SL at 90% GVL was 35.7% dry weight compared to 19.9% of MWL.

In another study on corn stover using GVL solvent, it was shown that almost 75.4% of the initial 14.3% lignin content was removed after 30 min reaction time at 150 °C, with a L:W ratio of 5:1 and H_2SO_4 of 150 mM (Luterbacher, Azarpira et al. 2015).

Also, birch as a wood feedstock was investigated (Fang, Sixta 2015), and gave promising delignification results. The reactions were carried out at 170 °C for 2 hours without the addition of acids. It can be seen from the below Fig. 20, that the highest delignification was achieved at 50% GVL with almost 5% dry weight residual lignin in remaining in pulp. Also, agreeing with the previous reports (Wu, Liu et al. 2016), higher GVL content did not yield better delignification, thus confirming the necessity of the presence of adequate amount of water needed for hydrolysis.

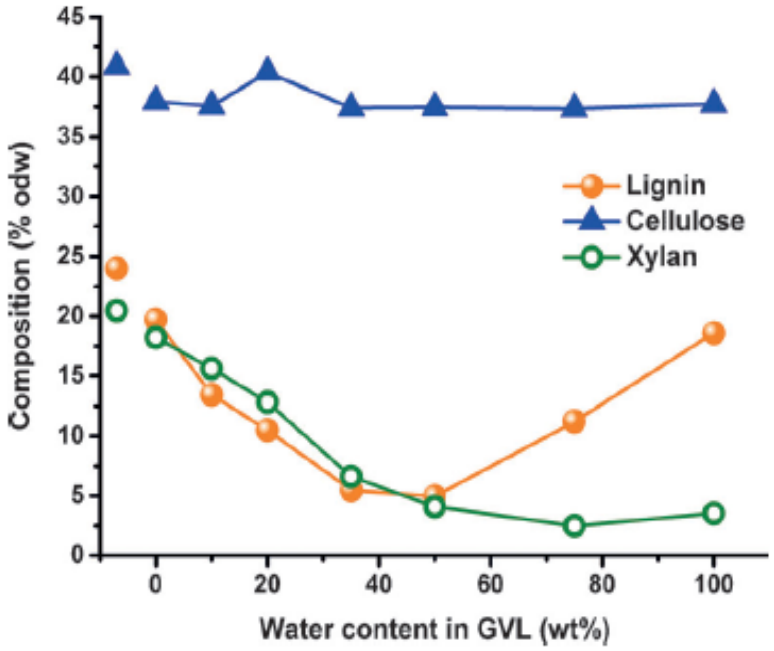


Fig. 20 *Pulp components yield in birch wood GVL/water hydrolysis (Fang, Sixta 2015)*

Table 4 shows the effect of acids in organosolv treatments. The addition of 0.05 M H_2SO_4 reduced the residual lignin in pulp from 5.5% to 3% at even lower reaction temperature of 130 °C. Subsequently at 150 °C and 0.04 M H_2SO_4, the found residual lignin was the lowest with only 1.7% residual lignin.

Table 4 Components yield of different GVL/water ratio with different H_2SO_4 concentrations and temperatures. (Fang, Sixta 2015)

Entry	Sample[a]	Major components [wt %]							
		cellulose		hemicellulose		lignin			furfural
		pulp	liquid	pulp	liquid	pulp	liquid	precipitate	liquid
1	birch sawdust	40.9		23.8		24.0			–
2	35%–170 °C–0 M–120 min	37.4	0.8	7.8	10.7	5.5	11.5	7.4	1.0
3	50%–170 °C–0 M–120 min	37.5	1.1	4.9	11.5	5.0	10.9	8.0	2.4
4	50%–130 °C–0.05 M–120 min	37.1	1.6	4.0	14.1	3.0	11.0	9.0	0.4
5	50%–170 °C–0.01 M–45 min	36.4	1.4	3.3	16.4	3.4	10.0	10.5	0.7
6	35%–170 °C–0.01 M–45 min	36.1	0.8	7.1	14.6	2.8	12.9	10.4	0.2
7	50%–150 °C–0.05 M–45 min	34.5	2.7	1.7	17.2	1.9	11.9	9.4	1.3
8	50%–150 °C–0.05 M–30 min	34.6	2.3	2.6	17.2	2.4	9.8	10.0	0.7
9	50%–150 °C–0.04 M–45 min	33.4	2.6	2.0	16.9	1.7	10.4	10.9	0.9

[a] The samples are named as water content in GVL–temperature–concentration of sulfuric acid–fractionation time.

The above data can be compared to water hydrolysis of birch wood in absence of GVL (Borrega, Nieminen et al. 2011), where birch wood was hydrolyzed and the yield products were determined. Even at higher temperature, 180 °C, significantly higher residual lignin is still present in pulp, 57%

of the initial 26% (14.8% lignin dry weight). This value, when compared to the 5% reported before with the use of 50% GVL, shows the added role of GVL in wood delignification. A similar value to the 5% reported previously was found when the temperature was further increased as high as 240°C, the maximum delignification reported was 22% which is equivalent to 5.7% lignin dry weight. Residual lignin curves are illustrated in Fig. 21.

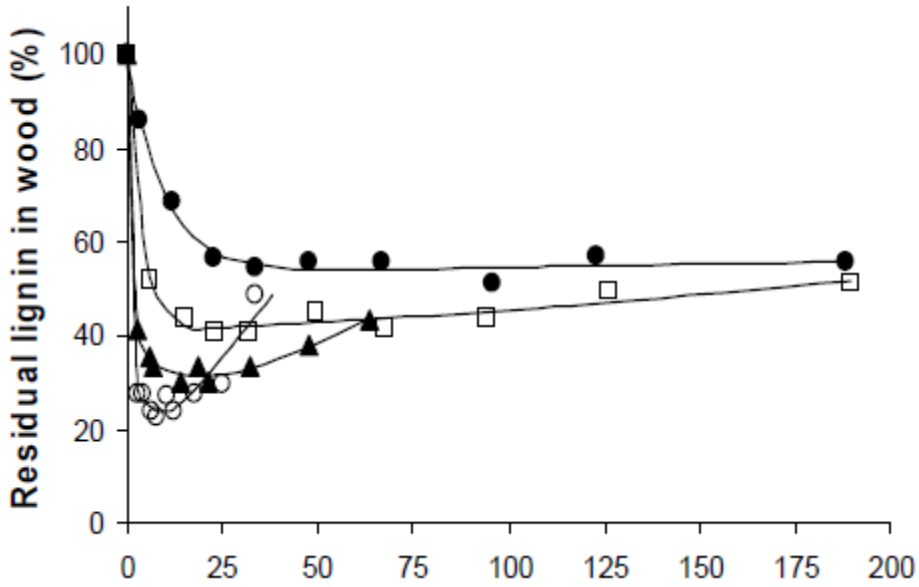


Fig. 21 *Residual lignin from birch wood autohydrolysis at 180 °C, 200 °C, 220 °C and 240 °C (Borrega, Nieminen et al. 2011)*

The kinetics for the delignification of the autohydrolysis reactions was also reported. The highest rate constant was found at the highest temperature 240 °C with 2.538 min^{-1}, and the delignification was much slower at 180 °C with 0.105 min^{-1}. On the other hand, condensation reactions are highly promoted at higher temperatures. The condensation rate constants were also higher at 240 °C than at 180 °C (Borrega, Nieminen et al. 2011).

GVL kinetics in literature

As shown in the previous studies, the presence of GVL in the solvent improves the hydrolysis of biomass. On the kinetics side, the reaction rate constants of the hydrolysis were tested and reported for cellobiose (Mellmer, Alonso et al. 2014). The study confirms that the presence of GVL in biomass hydrolysis aided by acid catalysis can significantly decrease the required catalyst concentration up to 5-fold while maintaining similar hydrolysis profiles to that of pure H2O. (Mellmer, Alonso et al. 2014, Fang, Sixta 2015).

Furthermore, faster reaction kinetics were shown in favor of GVL/H2O usage over pure water. It is shown that the rate constants for cellobiose hydrolysis has increased by more than 7.5-fold when hydrolyzed with GVL/H2O of ratio 4:1 than when water is used (Mellmer, Alonso et al. 2014).

From the below Table 5 it can be noticed that the rate constants increase as the ratio of GVL/H2O increases. The presence of water in the reaction is essential nonetheless since the role of the GVL in the reaction mechanisms is directed towards the stabilization of the acidic proton relative to protonated transition states and the presence of the hydronium ions from water is responsible for cleaving the β(1→4) glycosidic bond (Mellmer, Alonso et al. 2014). The GVL effect was found to increase the reaction rates and decrease the activation energy required for hydrolysis (Mellmer, Alonso et al. 2014).

Fig. 22 demonstrates the increase of the reaction rates of cellobiose hydrolysis in presence of H_2SO_4 as a catalyst, plotted on the left axis for different GVL/H2O ratios (represented by the lower curve). On the other axis, the apparent activation energy is plotted showing decrease in the required energy as the ratio of GVL/H2O increases. In Table 6 the activation energy has decreased to 81 KJ mol-1 for GVL/H2O of 4:1 down from 131 KJ mol-1 for water (Mellmer, Alonso et al. 2014).

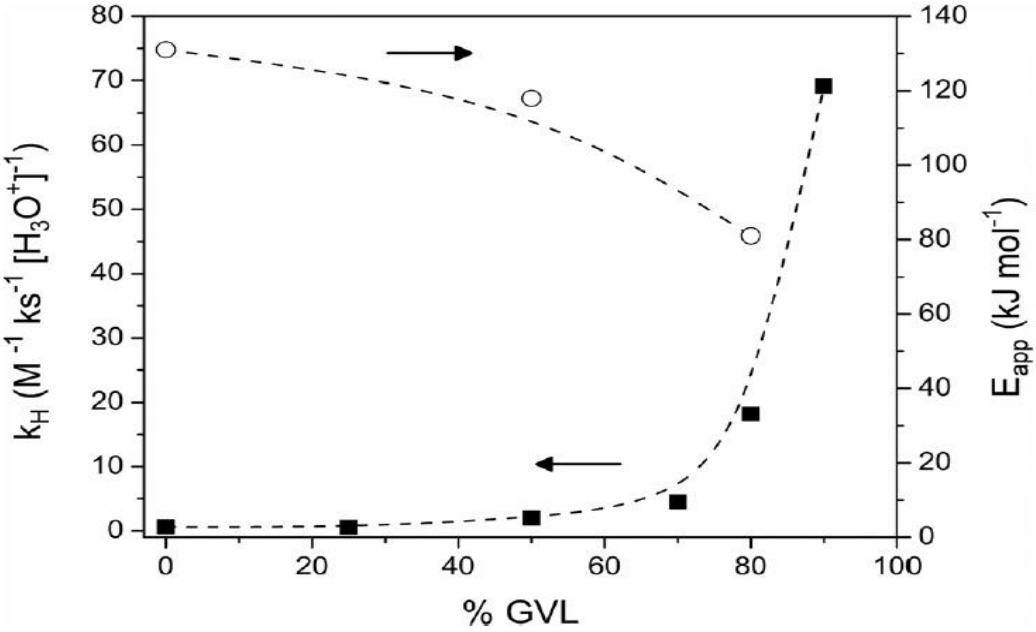


Fig. 22 *Cellobiose hydrolysis rate constants (square; left axis) and apparent activation energies (circle; right axis) versus GVL/water content (Mellmer, Alonso et al. 2014)*

Table 5 Rate constants of acid-catalyzed hydrolysis of cellobiose and maltose in water and GVL/water solvents using H_2SO_4 as catalyst (Mellmer, Alonso et al. 2014)

Solvent system	Reactant	Temp (K)	k_H (M^{-1} ks^{-1} $[H_3O^+]^{-1}$)
GVL–H_2O (4 : 1)	Cellobiose	393	8.9 ± 0.41
H_2O	Cellobiose	403	0.61 ± 0.051
H_2O	Maltose	403	0.81 ± 0.069
GVL–H_2O (1 : 3)	Cellobiose	403	0.54 ± 0.029
GVL–H_2O (1 : 1)	Cellobiose	403	2.0 ± 0.055
GVL–H_2O (2.33 : 1)	Cellobiose	403	4.5 ± 1.1
GVL–H_2O (4 : 1)	Cellobiose	403	18 ± 1.9
GVL–H_2O (4 : 1)	Maltose	403	19 ± 3.1
THF–H_2O (4 : 1)	Cellobiose	403	22 ± 3.3
Dioxane–H_2O (4 : 1)	Cellobiose	403	9.1 ± 1.5
GVL–H_2O (9 : 1)	Cellobiose	403	69 ± 9
GVL–H_2O (4 : 1)	Cellobiose	413	29 ± 6.1
H_2O	Cellobiose	418	2.2 ± 0.17
GVL–H_2O (1 : 1)	Cellobiose	418	8.6 ± 1.4
H_2O	Cellobiose	433	9.1 ± 1.5
GVL–H_2O (1 : 1)	Cellobiose	433	22 ± 3.4

Table 6 Apparent activation energies for acid-catalyzed hydrolysis of cellobiose and the conversion of glucose and xylose in water and GVL/water solvents (Mellmer, Alonso et al. 2014)

Solvent system	Reactant	E_{app} (kJ mol^{-1})
H_2O	Cellobiose	131
H_2O	Glucose	135
H_2O	Xylose	138
GVL–H_2O (1 : 1)	Cellobiose	118
GVL–H_2O (4 : 1)	Cellobiose	81
GVL–H_2O (4 : 1)	Glucose	138
GVL–H_2O (4 : 1)	Xylose	135

3. Materials and methods

3.1. Materials and practical work methodology

Scots pine (*Pinus sylvestris* L.) from southern Finland was chipped and screened according to SCAN-CM 40:01. Chips were frozen until further use. GVL of 98% wt. was available from Sigma-Aldrich Oy. All the reactions were conducted using Anton Paar Monowave 300 reactor 30 mL vials (Fig. 23).

Pretreatment of wood chips was first carried out by air drying the chips over two nights then milling using Wiley mill. The milling step is essential to increase the wood particles surface area accessible to the reaction. Thus, decreasing the reaction time needed. After milling, the milled wood was screened using 0.125 mm mesh in a shaker over 2 hours duration. Finally, 1.5 g of the milled wood was weighted as samples prior to the reaction.

The dry matter content of the milled wood was determined by drying two samples of the milled wood overnight in the oven at 105 ºC. The weight of the samples was recorded before and after drying. The dry matter content is the percentage of the dry weight over the initial wood weight.

The solvent samples were prepared based on L:W ratio of 10:1. The sample volume was therefore 15 ml per 1.5 g of milled wood. For the delignification potential of pinewood using GVL solvent, a series of GVL/H2O samples were prepared starting from 0% wt. GVL (pure water), 10%, 20%, 35%, 50%, 60%, 75% and 98%. The weight of each sample was recorded. The cooking reactions were carried out in duplicates for each ratio of GVL/H2O. The cooking was done in 30 mL vials in the monowave reactor. The reaction conditions were set to be 180 °C for 120 min. In addition, two other sets of runs were made at 50% and 60% wt. GVL. The purpose of the additional tests is to separately test the effect of increase in temperature and increase in residence time on delignification. One set was set at 200 ºC and 120 min, denoted with (H) symbol, and the other was 180 ºC and 150 min, denoted with (L) symbol. Full reaction conditions are shown below in Table 7 and Table 8.

Table 7 Reaction conditions for milled pine wood at GVL-H2O

Weight, g	**Particle size, mm**	**L:W**	Temp, °C	**GVL % wt.**							
1.5	0.125	10:1	180	0	10	20	35	50	60	75	98

Table 8 (H) and (L) reaction conditions

	50H	**60H**	**50L**	**60L**
Temp, °C	200	200	180	180
Time, min	120	120	150	150

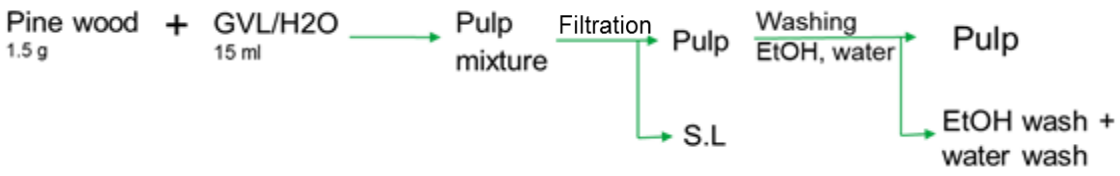
For the study of kinetics, using the same L:W ratio and at 60% wt. GVL, three temperatures were chosen for the reaction to describe the delignification and the sugars degradation in pine wood. The temperature points are 180 ºC, 195 ºC and 210 ºC. A series of reactions were carried out at different reaction times for each temperature. The series reaction time proceeded until the decrease in pulp yield was almost stable and had no variation with reaction time. The chosen reaction durations and conditions are shown in Table 9. Note that the wood particle size used in the 210 °C series is 0.2 mm. Please view the observations and recommendations section for more details.

Table 9 Reaction conditions for the time series for milled pine wood treatment with GVL-H2O solvent

Weight, g	**Particle size, mm**	**GVL %**	**L:W**	Temp, °C	**Time, min**							
1.5	0.125	60	10:1	180	5	10	20	45	60	90	120	180
1.5	0.125	60	10:1	195	5	10	15	20	25	30	45	60
1.5	0.2	60	10:1	210	2	5	10	15	20	25	30	45

Following the reactions, as shown in Scheme 2, the reaction mixtures were readily poured in a 30 ml crucible and the spent liquor was filtered with the aid of air vacuum. Then, pulp was washed with 15 mL of 50% weight ethanol solution to ensure the entrapped spent liquor and lignin are washed away. Finally, washing of the entrained ethanol solution from the pulp was done with 200 mL of deionized water.

The pulp samples were dried overnight in the oven at 105 °C. Then the weight was measured and recorded. The weight of spent liquor and ethanol wash of each reaction was also measured and recorded. In addition, the pH of the produced spent liquor was determined using digital pH meter. Lastly, the spent liquor and the ethanol wash were kept in the freezing room at -7 ºC. The washing water was stored in the cooling room.



Scheme 2 Experiments protocol

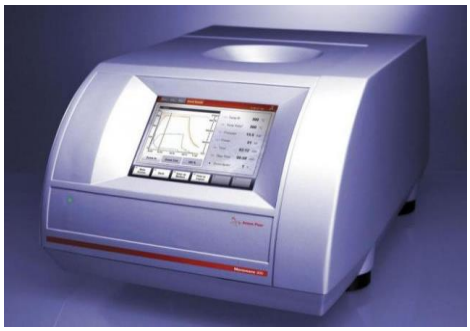


Fig. 23 *Anton Paar Monowave 300 reactor*

3.2. Analysis and characterization

Pulp

The amount of carbohydrates and residual lignin remaining in the pulp after cooking were analyzed according to the 2-step hydrolysis method described in the NREL/TP-510-42618 standard. The first hydrolysis step is achieved with 72% H2SO4 with acid-to-material ratio of 10 mL/g, at 30±3°C, for 60±5 minutes. The second hydrolysis step is done with 4% H2SO4 with acid-to-material ratio of 300 mL/g, at 121±1°C, for 60 minutes.

The hydrolysis mixture is filtered and the liquid samples were prepared for analysis of the existing monosaccharides. The sugars were analyzed using high performance anion exchange chromatography (HPAEC-PAD) in a Dionex ICS-3000 system, equipped with CarboPac PA20 column. The detected monosaccharides consisting of arabinose, galactose, glucose, xylose and mannose could be traced back to the polysaccharides, cellulose and hemicelluloses. The values of the polysaccharides are estimated using Janson formulae (Janson 1970). The description of the formulas and the variables used are shown in Appendix 1.

The lignin content in pulp consists of two fractions: acid-soluble lignin and acid-insoluble lignin (Klason lignin). The Klason lignin was determined gravimetrically and the acid-soluble was determined by measuring the absorbance at a wavelength of 205 nm using Shimadzu UV-2550 spectrophotometer. An extinction coefficient of 148 L/(g.cm) was used for quantification of ASL.

Spent liquor

The carbohydrate and lignin content in the spent liquors were analyzed in accordance to the method described in the NREL/TP-510-42623 standard. The monomeric sugars were determined by direct injection in the HPAEC-PAD, the oligomeric sugars were determined by difference after hydrolysis at 121±1°C for 60 minutes, with sulfuric acid concentration of 4%.

As for lignin, UV-Vis spectrophotometry (Shimadzu UV-2550 spectrometer) was used to determine the lignin content. Lignin in the spent liquor was first diluted by 35% ethanol to avoid any precipitation while performing the analysis. The used wavelength is 205 nm and the extinction coefficient is 148 L/(g.cm).

Washing filtrates

Sugars were assumed to be completely filtered with the spent liquor, thus, no sugar analysis was carried out for the washing liquors. The liquor from washing filtrates was only analyzed for lignin content using the UV-Vis spectrophotometer (Shimadzu UV-2550) with the same methodology to dilute with 35% ethanol.

Acids and furfurals

The content of furanics (furfural and HMF) and organic acids (formic acid, acetic and levulinic acid) in the spent liquor was determined by high performance liquid chromatography in a Dionex UltiMate 3000 (Dionex, Sunnyvale, CA, USA) device equipped with Refractive Index (RI) and UV diode array detectors and HyperREZ XP Carbohydrate Ca+ column 7.7×300 mm (Thermo Scientific, Waltham, MA, USA). The eluent was 0.005 mol/L sulfuric acid. The column temperature and the RI detector temperature were set to 70 ºC and 55 ºC, respectively.

3.3. Modelling

A model was constructed for the hydrolysis reactions of wood components (lignin, cellulose, xylan and GM) based on the components residual values in pulp. For simplification, the hydrolysis reactions were assumed to follow a first order reaction kinetics model. The residual values of lignin as well as the polysaccharides were plotted separately and fitted to an exponential model. Modelling and determining the rate constant of each reaction was done using Wolfram Mathematica 10.3 non-linear curve fitting functions.

4. Results and discussion

Analysis of the original milled pinewood showed the initial wood constituents. As shown in Fig. 24, 42.6% of the wood is formed of cellulose, followed by hemicelluloses with 24% in total, of which 16% is glucomannan and 8% is xylan. On the other hand, lignin is found to be 28.4% of the original wood with the 4.5% rest as extractives. Please note that the extractives content was not analyzed but assumed to make up for the remaining percentage.

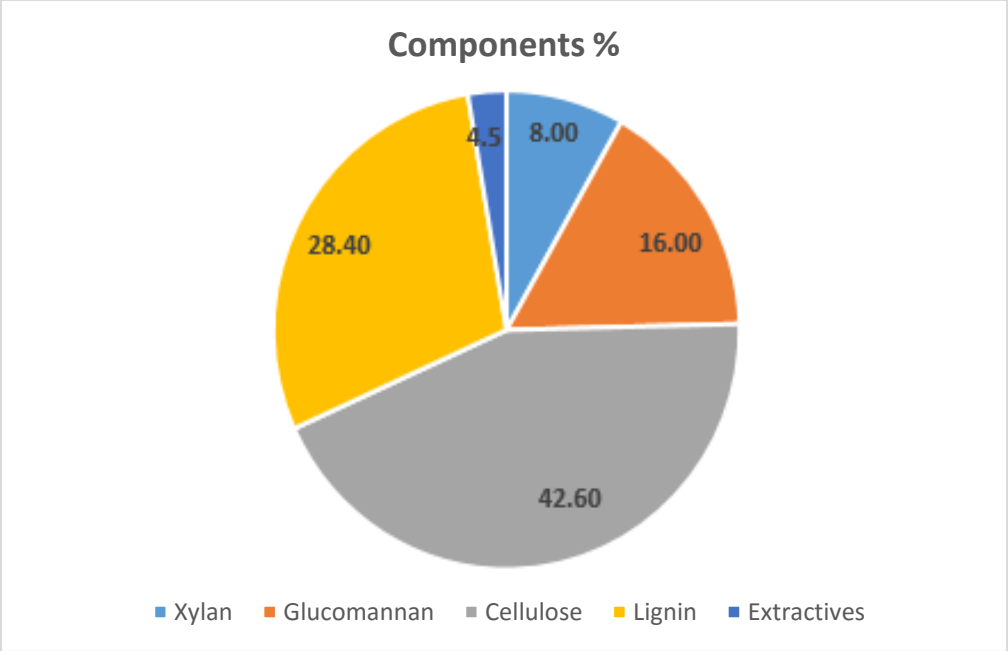


Fig. 24 *Pine wood components*

4.1. Cooking with GVL-H2O series

It can be observed from the below Fig. 25, that the pulp yield was reduced from 70% at 0% GVL to minimum of 59.7% and 60.2% at 35% and 50% GVL, respectively. Then the yield increased as the GVL wt. % increase in the solvent. The pulp yield can be explained by studying the residual cellulose, hemicelluloses and lignin yield presented in Fig. 26. Observed from the graph, that cellulose yield is not significantly affected by the increase of GVL content, it can be seen that cellulose yield is stable around 39% at GVL content starting from 0% wt. to 75% wt. If the GVL wt % would be further increased, then due to the absence of hydronium ions, the hydrolysis reactions affecting cellulose are almost non-existing, resulting in almost no change in cellulose yield at 98% GVL compared to the initial 42% cellulose content in wood.

On the other hand, hemicelluloses and lignin are highly affected by the GVL presence. It is clear that hemicelluloses follow an increasing trend with the increase of GVL content. With pure water, only 4% of total hemicelluloses were to remain in the pulp when the most of xylan and glucomannan are hydrolyzed. This percentage increase to 10.8% at 60% GVL and 25.2% at 98% GVL. As for lignin, the delignification intensity is dependent on the GVL content. In pure water, only minor amount of delignification was found. The optimum delignification can be observed at 50% and 60% GVL while it decreases at higher GVL %.

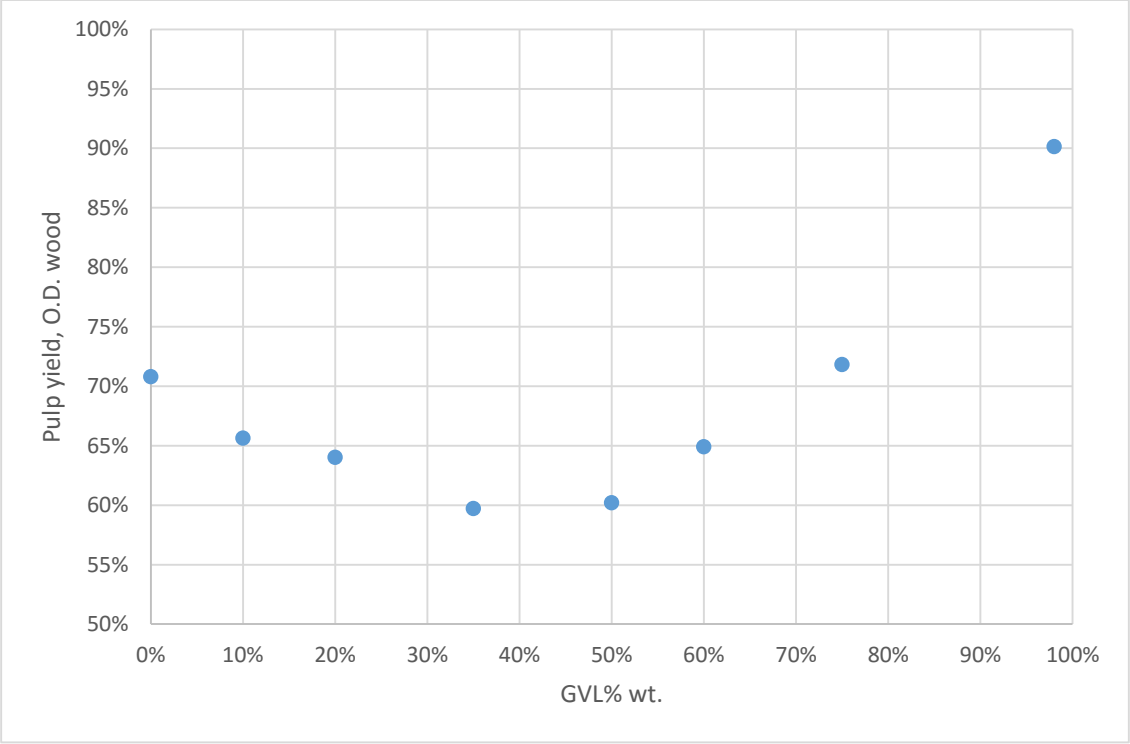


Fig. 25 *Pulp yield for the GVL/H2O series at 180 °C and 120 min*

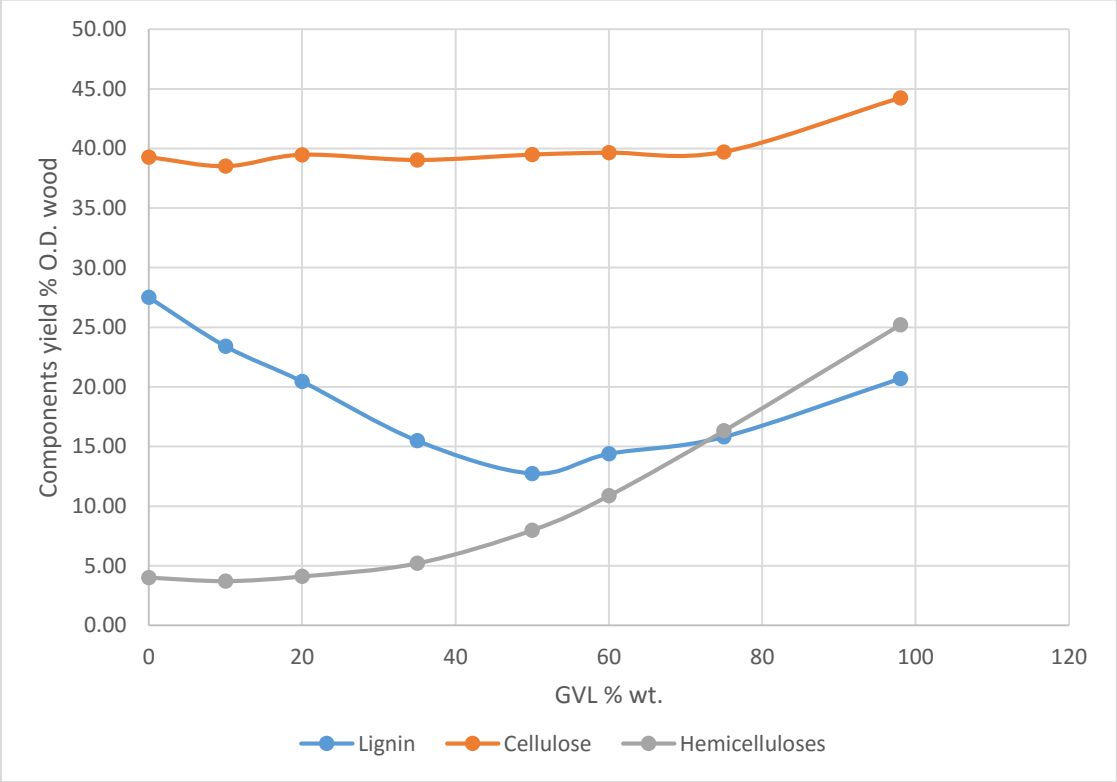


Fig. 26 *Cellulose, hemicellulose and lignin yields during the treatment*

Table 10 Pulp components for the GVL-H2O series on O.D. pulp basis

	%GVL	0	10	20	35	50	60	75	98
% O.D pulp	Xylan	2.84	3.05	3.48	4.4	5.75	6.33	6.99	9.49
	GGM	2.82	2.61	2.92	4.3	7.49	10.42	15.7	18.46
	Cellulose	55.48	58.67	61.67	65.36	65.59	61.08	55.32	49.07
	Lignin	38.87	35.67	31.92	25.93	21.17	22.16	21.98	22.98

From the above figure and Table 10 it can be seen that maximum delignification was achieved at 50% and 60% wt. GVL with 21.17% and 22.16% O.D. pulp respectively, agreeing with the study reported in the literature section on birch wood (Fang, Sixta 2015). Contrarily for 0%, 10% and 20% wt. GVL, the delignification is not as significant with residual lignin of 33.87%, 35.67 and 25.93% O.D. pulp respectively. The results show that the optimum GVL/H2O for milled pinewood lies in the range of 50% to 60%. However, the residual lignin values for pine wood after treatment is higher than that reported for eucalyptus or birch wood. At the same reaction temperature and duration, it was found that the residual lignin content in milled eucalyptus is 7.9% and 7.1% O.D. pulp at 50% and 60% wt. GVL respectively (Le et al. 2016).

Although hydrolysis reactions are acid catalyzed reactions, the presence of GVL and its ratio to water plays an essential role in these reactions. From the above Fig. 26, it is shown that the best delignification is achieved in 50% to 60% GVL. However, Fig. 27 shows that at these GVL contents the pH of the SL is not the lowest. SL from 10% to 35% GVL have lower pH than that at 50% and 60% GVL while still having higher lignin content in pulp. Thus, the content of GVL in the solvent is decisive in the delignification mechanism (MartinAlonso, Marcel R Gallo 2013, Mellmer, Alonso et al. 2014).

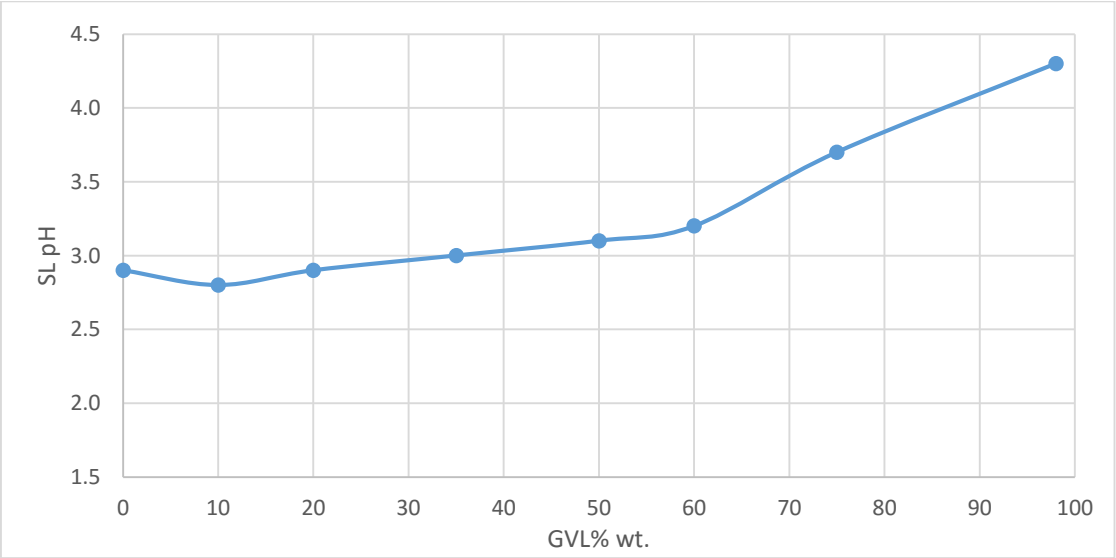


Fig. 27 *SL pH for the GVL/H2O series at 180 °C and 120 min*

Fig. 28 and Fig. 29 show pictures taken of the produced pulp and SL after the reactions with 0%, 20%,50% and 75% GVL. It can be observed that pulp produced at 50% GVL, where maximum delignification occurs, has the brightest color. Especially if compared to the pulp produced with 20% GVL. The same can be noticed with the SL samples.

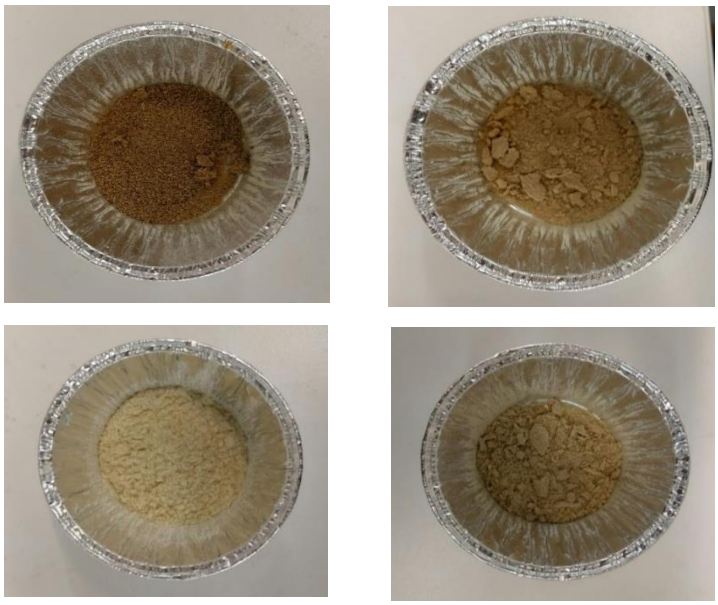


Fig. 28 *Pulp color and texture after treatment. (0% GVL; top left, 20% GVL; top right, 50% GVL; bottom left, 75% GVL; bottom right)*

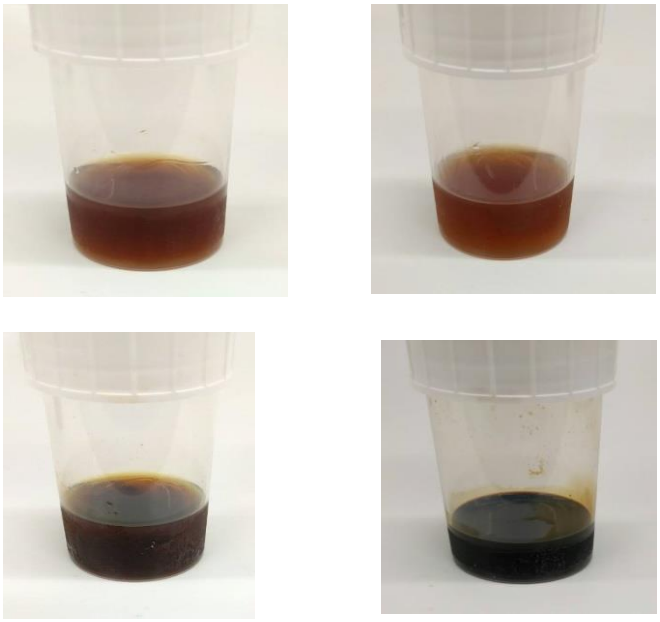


Fig. 29 *SL samples color after treatment. (0% GVL; top left, 20% GVL; top right, 50% GVL; bottom left, 75% GVL; bottom right)*

For the 200 °C and 120 min (H), and 180 °C and 150 min (L) runs at 50% and 60% GVL, the polysaccharides yields are observed in the below Table 11. The table showed increase in the hemicelluloses hydrolysis induced reactions at (H) more than that at (L), with total hemicelluloses content of 2.6% and 5.4% at 50% H and 60% H, compared to 5.1% and 10.6% at 50% L and 60% L respectively. On the contrary, limited decrease in the residual cellulose content in the pulp after the (H) and (L) runs was noticed. As in the hemicelluloses, higher degradation of cellulose could be observed in the (H) runs, with cellulose of 36.7% at 50% GVL and 37.6 at 60% GVL. The degradation reactions were less pronounced in the (L) runs, with 37% and 39% residual cellulose at 50% and 60% GVL. The above results explain that hydrolysis and degradation reactions are more favored in higher temperatures than in longer reaction times (Parajo, Alonso et al. 1995).

Similarly, lignin in pulp from the (H) reactions was less than that of the (L), pointing out to more cleavage in the α-O-4 and β-O-4 bonds at higher temperatures than longer times. As shown in Table 11, residual lignin was 7.5% and 5.9% at 50% and 60% (H) conditions, compared to 10% and 14.7% at 50% and 60% (L) conditions, respectively.

The above polysaccharides and lignin values can be added up to describe the pulp yield from the (H) and (L) runs. It is clear that due to the higher hydrolyzation reactions occurring at (H) runs, the pulp yield is less than that obtained from (L), with 47% and 49% yield at 50% and 60% (H) respectively, compared to 62% and 64% at (L) respectively (Table 11).

Table 11 Pulp components yield on dry wood basis for the (H) and (L) runs

% GVL	50	60	50H	60H	50L	60L
Hemicelluloses	7.98	10.87	2.61	5.40	5.16	10.60
Cellulose	39.49	39.65	36.70	37.62	36.90	39.02
Lignin	12.73	14.39	7.49	5.87	10.04	14.69
Pulp yield	60	65	47	49	62	64

The above results are also reflected in the SL mono-sugars to total sugars ratio. At higher temperature, more hydrolyzation and degradation reactions occur, resulting in more mono-sugars in the SL. Fig. 30 displays the percentage of mono-sugars existing in SL to total sugars that are acquired from the NREL/TP-510-42623 standard method. The results illustrates that more mono-sugars are found in the (H) runs than the (L) runs.

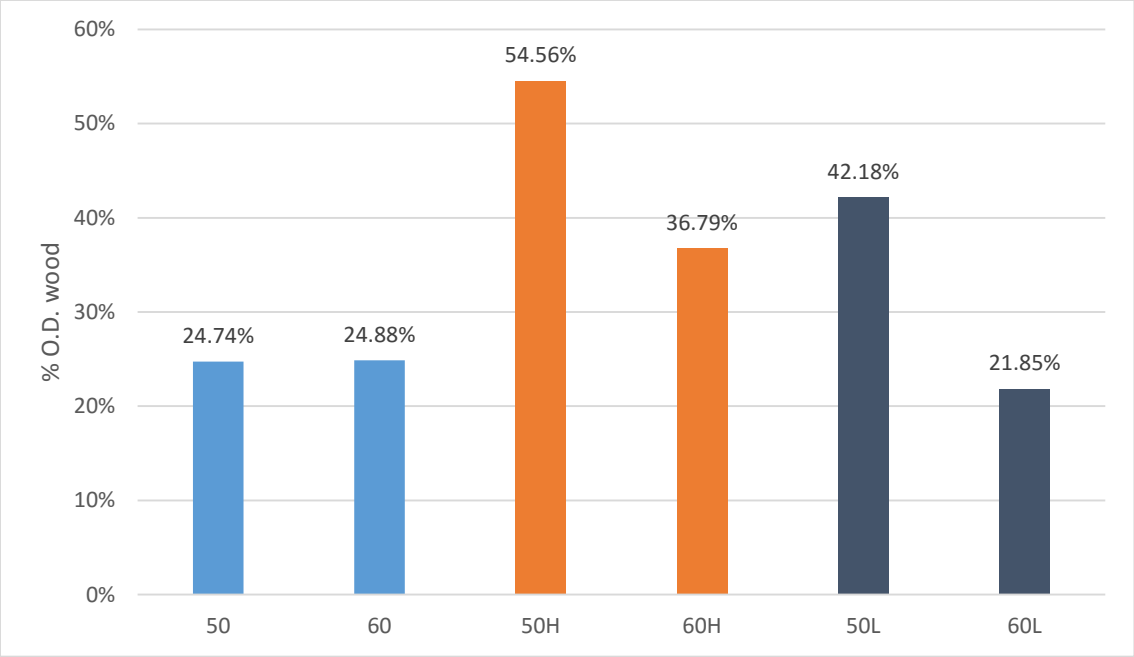


Fig. 30 *Mono-sugars to total sugars percentage in S.L. for 50% and 60% wt. GVL in different reaction conditions*

The generation of acids and furans is shown in Fig. 31 and Fig. 32. Starting with the acids formation, acetic acid is mainly formed from the cleavage of the acetyl groups attached to the hemicelluloses backbone chain. These reactions are promoted by higher temperatures and longer residence time (Iakovlev, You et al. 2014). As for formic and levulinic acids, they are primarily produced from the hydration reactions of HMF. Thus, at higher temperatures, less hydration reactions are possible yielding less formic and levulinic acids compared to reactions for longer duration where hydration reactions are enforced. Furans, on the contrary, are generated from degradation reactions of C6 polysaccharides, GM and cellulose to HMF, and C5 polysaccharides, xylan to furfural. The effect of higher temperature (H) clearly promote the dehydration reactions and the formation of HMF and furfural (Iakovlev, You et al. 2014). Longer reaction time (L) also increase the furfurals production, but the effect of temperature was significantly higher than that of time.

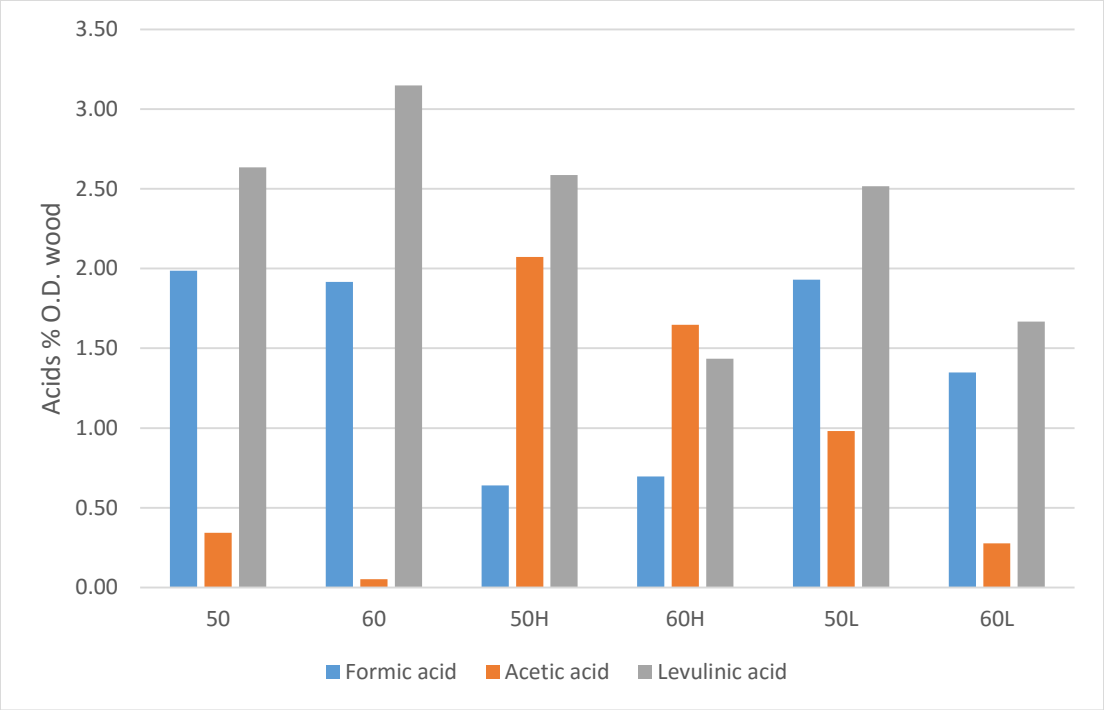


Fig. 31 *Acids formation in S.L. for 50% and 60% wt. GVL at different reaction conditions*

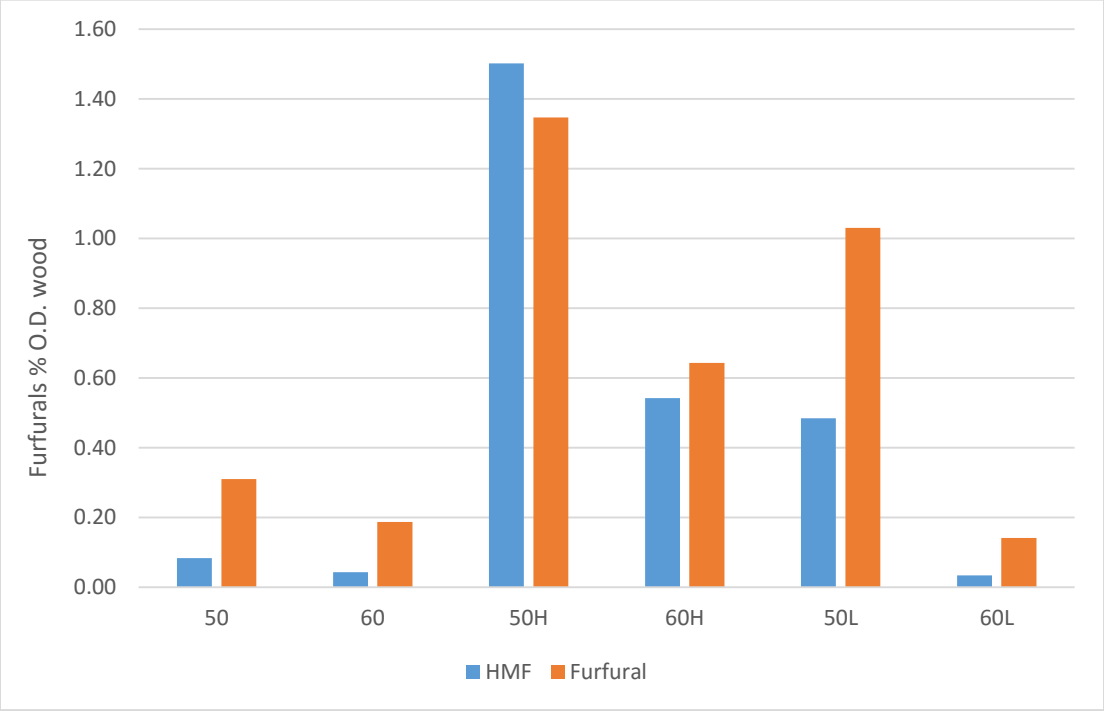


Fig. 32 *Furfurals content in S.L. for 50% and 60% wt. GVL at different reaction conditions*

Overall mass balance calculations for each trial were also conducted to determine the overall value of each constituent (cellulose, xylan, GGM and lignin) after the reaction. The values of the

compounds found in pulp, spent and washing liquors were traced back to the main polysaccharides and lignin. Cellulose consisted of cellulose in pulp and fraction of the glucan detected in spent liquor. HMF, acetic acid, formic acid, levulinic acid, galactan and mannan in liquor, along with GGM in pulp, formed the overall amount of GGM. Furfural in spent liquor along with the amount of xylan calculated in spent liquor and pulp formed the overall xylan amount. Finally, the overall value of lignin is the sum of ASL and Klason lignin in pulp, lignin in SL and washing liquor lignin. Values of the components mass balance are included in Appendix 2, Table 17, while the overall mass balance in the GVL-H2O series are summarized in Table 12.

The total values are the sum of the overall values of xylan, GGM, cellulose and lignin. It can be observed that the values of the total in the 50H and 60H samples, at 200 °C, are less than the average of other runs at 180 °C. The difference in the figures is interpreted by the loss reactions that occur with increasing temperature, yielding unknown and undetected compounds.

Table 12 Overall mass balance of the GVL-H2O trials

	%GVL	Wood	0	10	20	35	50	60	75	98	50H	60H	50L	60L
% O.D.wood	Xylan	8	5.9	5.8	5.7	5.8	6.1	5.6	5.7	8.6	5.3	5.2	5.6	5.7
	GGM	16.1	13.6	13	13.3	13.8	15.3	15.5	15.8	17.5	8.2	8.7	12.4	13.4
	Cell.	42.6	42.2	41.6	42.4	41.4	41.7	40.9	40	44.2	38.6	39.5	39.1	40.5
	Lignin	28.4	28.3	28.3	26.8	24.3	24.1	26.3	30.2	27.7	24.2	21.7	23.7	27.8
	Total	95.3	90	88.7	88.2	85.3	87.2	88.3	91.7	98	76.3	75.1	80.8	87.4

4.2. Cooking with time series

The second section of the thesis is aimed to study the kinetics of the reactions. For that purpose, three temperatures were chosen 180 °C, 195 °C and 210 °C. A total of 8 reactions at different hold-up durations were carried out at each corresponding temperature in order to obtain a comprehensible delignification curve, from which delignification rate constants (K) could be estimated.

Residual lignin in wood was determined as the sum of Klason lignin and acid-soluble lignin in Fig. 33. For the 180 °C, the lignin content decreased steadily over the first 60 min of reaction time. The lignin content dropped from the initial content, 28.4% to 19% after 60 min. Following that, the delignification rate is reduced through the remaining duration course, yielding 14.2% after 180 min. On the other hand, as expected, when temperature is raised to 195 °C, rapid delignification is observed during the first 45 min of reaction. Lignin content is decreased from 29% to 7.6% at 45 min. After that, minor lignin condensation reactions were noticed and the final lignin content after 60 min slightly rises to 8.2%. Furthermore, when 210 °C temperature is tested, delignification behavior was more intensive than at 195 °C. The reaction duration was shortened

from 60 min at 195 °C to 45 min at 210 °C. Final lignin at 210 °C is 5.5% after 45 min compared to 8.2% after 60 min at 195 °C. The same delignification behavior can be observed in the soluble lignin content, displayed in Fig. 34. Acceleration in the delignification kinetics was accompanied by the increase in temperature. For example, 10% lignin O.D. wood basis in SL was reached after 60 minutes at 180 °C, 20 minutes at 195 °C and only 9 minutes at 210 °C.

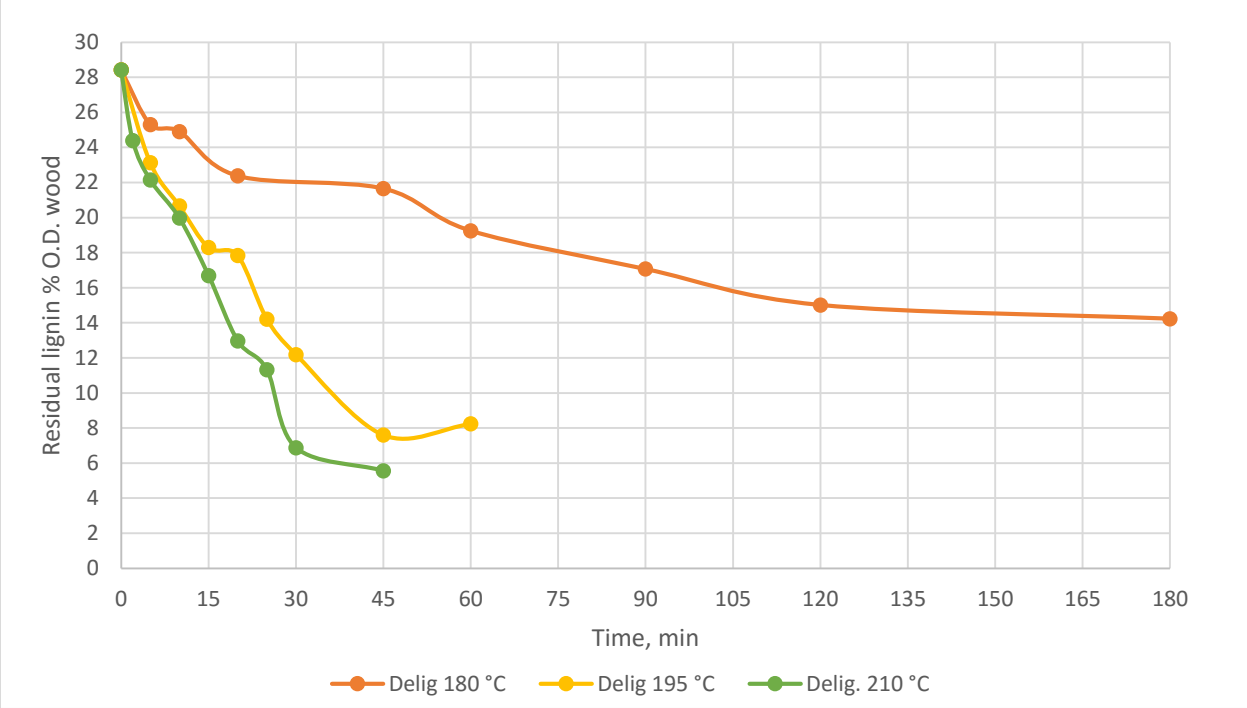


Fig. 33*Delignification curves for 180 °C, 195 °C and 210 °C*

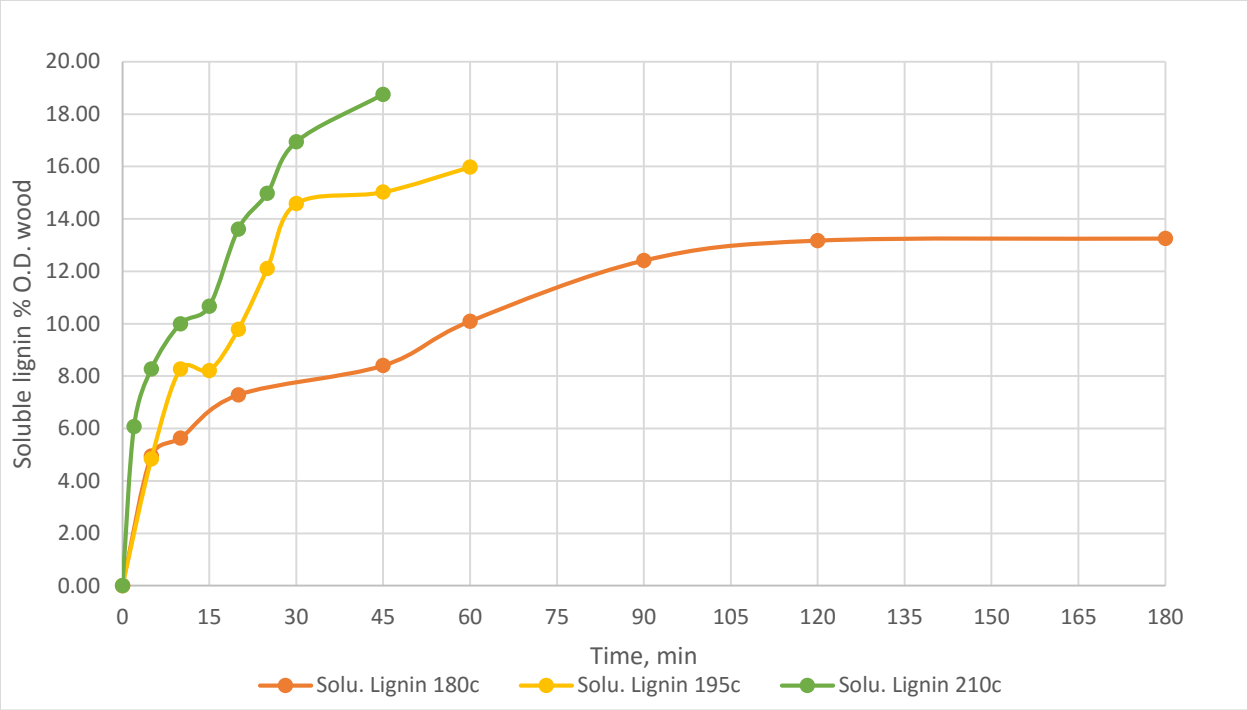


Fig. 34 *Soluble lignin for 180 °C, 195 °C and 210 °C*

Regarding the hemicelluloses, it is clearly visible that owing to their amorphous structures, both xylan and GM were readily hydrolyzed during the reactions. The below Fig. 35 and Fig. 36 show the effect of temperature on the rate of hydrolysis of xylan and GM, respectively. At 180 °C, 3.5% xylan from the initial 8% was found in pulp after 180 min. With increasing temperature, the residual amount reached 2.85% and 2.95% at 195 °C and 210 °C respectively. It is interesting to mention that the final xylan content in pulp after 60 min of reaction time, 2.6% at 195 °C was less than the amount found at 210 °C after 45 min. The same phenomena is observed with the hydrolysis of GM, from the initial 16%, the amount of residual GM in pulp is 3.9%, less than 4.6% after 45 min at 210 °C. However, at 180 °C, milder hydrolysis was detected with 6.8% after 180 min.

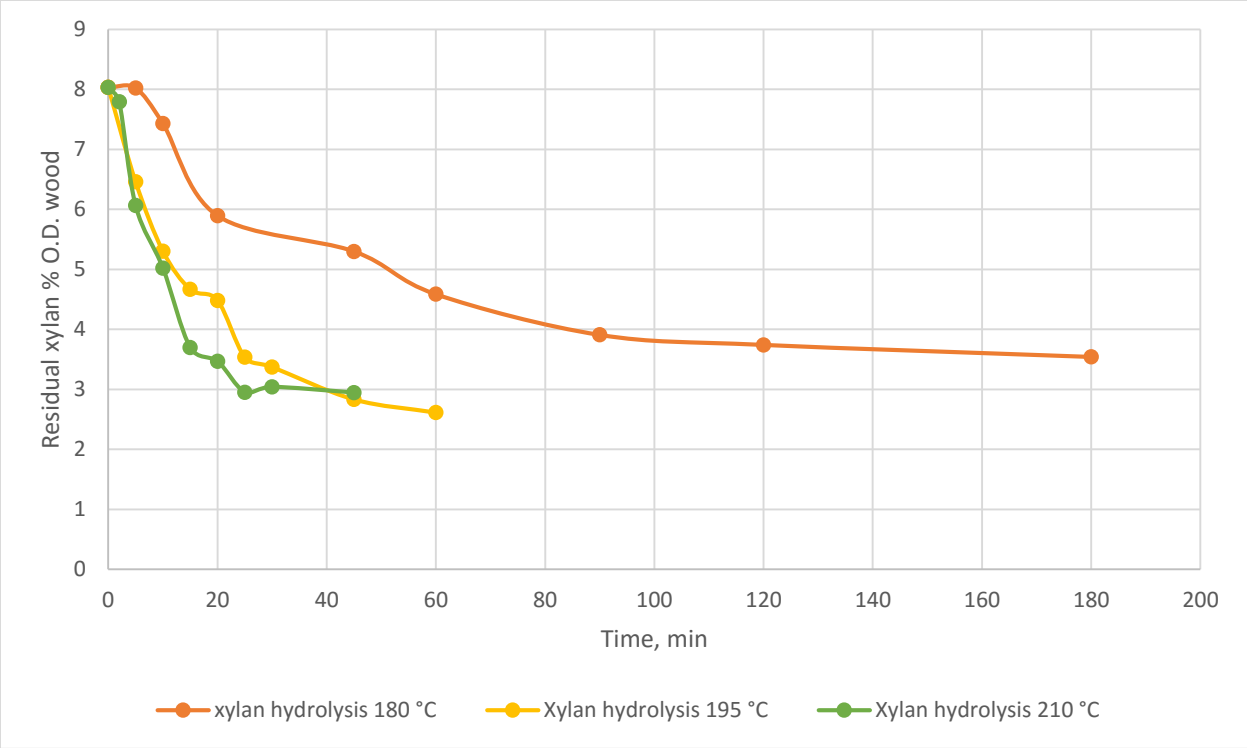


Fig. 35 *Residual xylan in pulp at 180 °C, 195 °C and 210 °C*

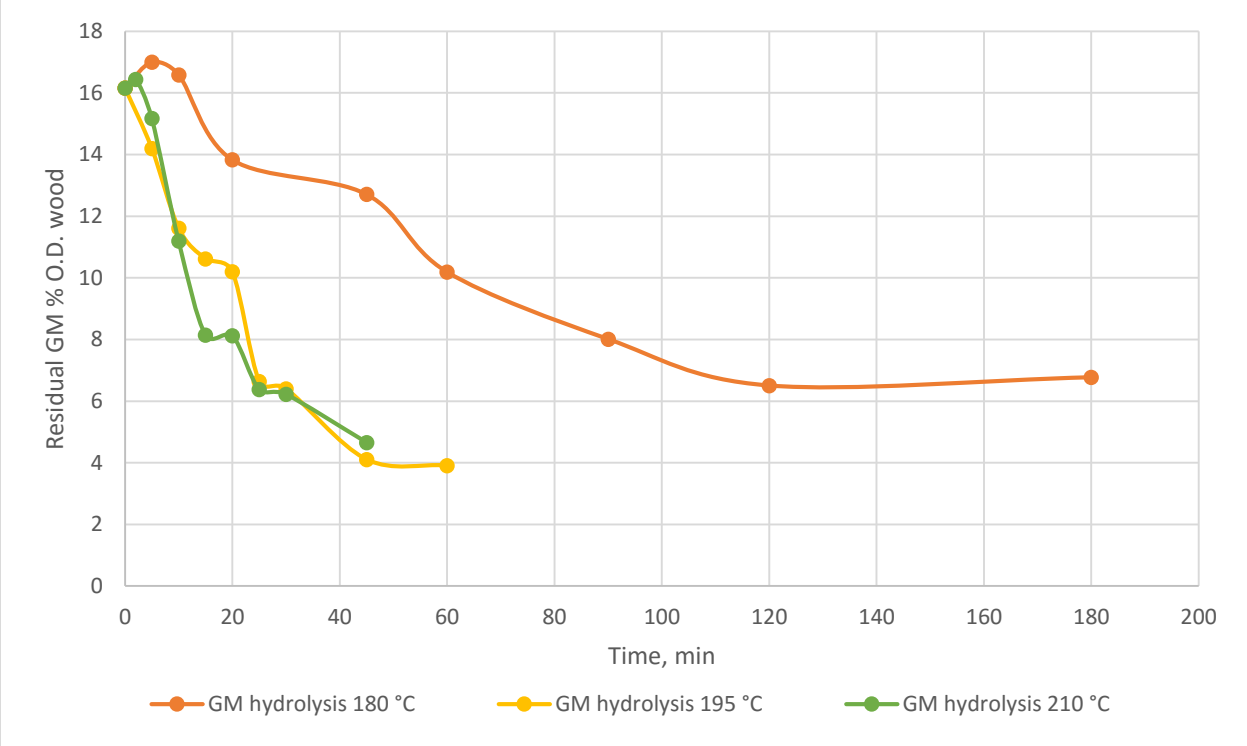


Fig. 36 *Residual GM in pulp for 180 °C, 195 °C and 210 °C*

Cellulose, on the other side, is more resistant to hydrolysis, since cellulose structure contains both amorphous and crystalline regions (Sjöström 1993c). In our case, as demonstrated in Fig. 37, only 3.6% losses in cellulose content were detected after 180 min at 180 °C with final content of 39% from initial 42.6%. As for the 195 °C and 210 °C, the sharp decline in cellulose content ceases after 25 min at 195 °C and 30 min at 210 °C with cellulose content of 35.5% and 35% respectively. Proceeding from these points, cellulose content is almost stable over the rest of the reaction time.

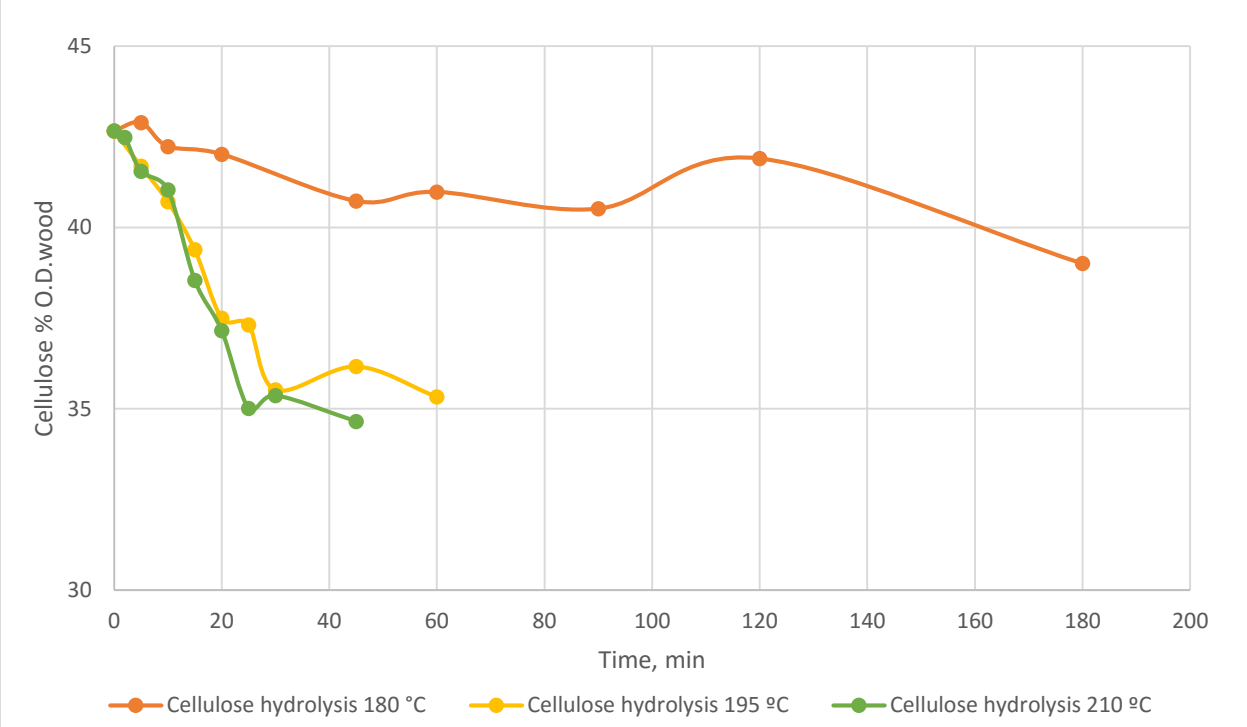


Fig. 37 *Residual cellulose in pulp for 180 °C, 195 °C and 210 °C*

For the time series, the generation of acids and furfurals was limited. The values of the detected HMF and furfural were less than 1% in all the tested temperatures. The small amounts can be related to the presence of GVL, as a hypothesis. Since if pure water was used instead and in the same reaction conditions, significant generation of furfurals and acids occurs (Borrega, Nieminen et al. 2011). The role of GVL in limiting the degradation and dehydration reactions is yet unknown. On the other hand, acids, levulinic and formic acids amounts decreased as the reaction is prolonged. The highest values of levulinic and acetic acids were detected in the beginning of the reaction, then decrease as the reaction proceeds, with values of less than 2% for levulinic acid and less than 1% for formic acid at the end of the reactions. Also, acetic acid amount was less than 1%.

For the purpose of determining the overall mass balances for each trial, the same methodology of tracing and converting the reaction products to their initial constituents, as in the above GVL-H2O series, was adopted. The fraction of the glucan detected in SL along with the yield cellulose in pulp formed the overall value of cellulose. Also, HMF, acetic acid, formic acid, levulinic acid,

galactan and mannan in liquor, along with GGM in pulp, formed the overall amount of GGM. Overall xylan value consisted of furfural in spent liquor along with the amount of xylan calculated in pulp and SL. Finally, the overall value of lignin is the sum of ASL and Klason lignin in pulp, lignin in SL and washing liquor lignin. Table 13, 14 and 15 show the overall mass balance corresponding to the time series at 180 °C, 195 °C and 210 °C. Detailed values of components mass balance are shown in Appendix 2, Table, 18,19 and 20.

Table 13 Overall mass balance of cellulose, xylan, GGM and lignin at 180 °C

180 °C	Time, min	5	10	20	45	60	90	120	180
% O.D.wood	Xylan	8.2	7.6	6.7	6.2	6.2	5.6	5.7	5.5
	GGM	21.8	21.3	19.4	17	15.7	13.8	13.2	13.8
	Cellulose	43	42.3	42.4	41.2	42	41.7	43.4	40.7
	Lignin	30.3	30.5	29.7	30.1	29.3	29.5	28.2	27.5
	Total	103.3	101.7	98.2	94.5	93.2	90.6	90.5	87.5

Table 14 Overall mass balance of cellulose, xylan, GGM and lignin at 195 °C

195 °C	Time, min	5	10	15	20	25	30	45	60
% O.D.wood	Xylan	6.6	6.2	5.7	5.6	5.2	5	4.4	4.1
	GGM	20.2	19.8	17.6	16.2	13.6	13.4	11.3	10.2
	Cellulose	41.8	41.2	40.2	38.3	38.6	36.7	37.9	36.9
	Lignin	28	28.9	26.5	27.6	26.3	26.8	22.6	24.2
	Total	96.6	96.1	90	87.7	83.7	81.9	76.2	75.4

Table 15 Overall mass balance of cellulose, xylan, GGM and lignin at 210 °C

210 °C	Time, min	2	5	10	15	20	25	30	45
% O.D.wood	Xylan	8.1	6.9	6.3	5.5	4.8	4.7	5	5.1
	GGM	21.7	21.3	18.6	17	15.3	14.4	13.8	11.8
	Cellulose	42.7	42.2	42.3	39.8	38.5	36.3	36.8	36.2
	Lignin	30.5	30.4	30	27.4	26.6	26.3	23.8	24.3
	Total	103	100.8	97.2	89.7	85.2	81.7	79.4	77.4

4.3. Lignin and polysaccharides modelling

Delignification rates were researched for the aim of studying the kinetics of delignification of pinewood with GVL. Various parameters play an important role in affecting how fast the delignification rate proceeds. Most important parameters are reaction temperature (also affects pressure), presence of catalyst, L:W ratio, initial lignin content in wood and wood particle size (Parajo, Alonso et al. 1995, Schols, Garrote et al. 2007). It is worth to note that all the reactions were done using the same L:W ratio, 10:1 with no catalyst tested.

For determining the delignification rates, first order reaction kinetics relation was assumed for simplification. The rate of reaction equation is expressed as.

$$\frac{dL}{dt} = -K_d * L$$

Where, dL/dt is the rate of delignification in lignin % ODW/ min.

K_d is the delignification rate constant in 1/min.

L is the lignin % ODW.

The above equation has a negative slope and is compensated by the negative sign. The equation is solved by obtaining the natural logarithms of the equation resulting in a linear relation.

$$Ln\ L2 = Ln\ L1 - K_d * t$$

Where, L2 is the lignin% after time t.

L1 is the initial lignin%

Based on the above equation, a delignification model explaining the delignification behavior over time at specific temperature could be built. The K_d values obtained were very similar when compared to K_d values from other solver tools, Wolfram Mathematica 10.3 non-linear curve fitting functions. The obtained curves in Fig. 38 could accurately describe the delignification data points.

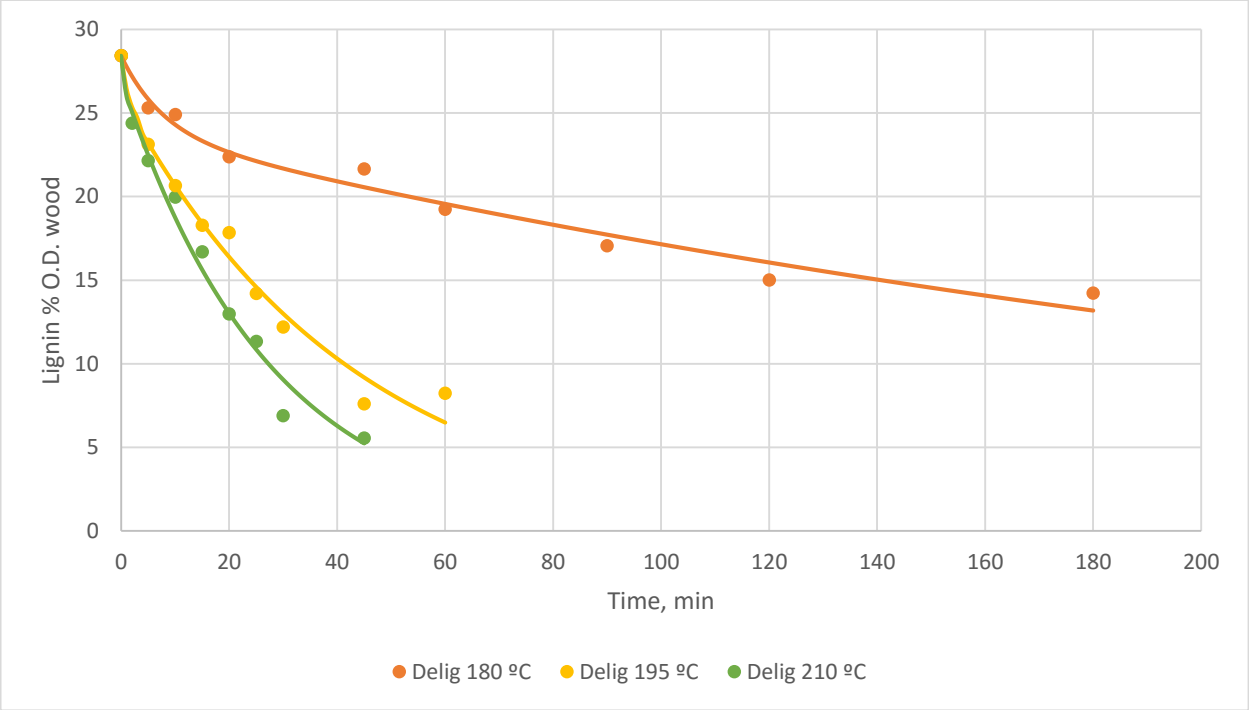


Fig. 38 *Delignification model with data fitting*

The acquired K_d values show increase in the rate constant as the temperature increases. The delignification rate constant was minimal at 180 °C with 0.0038 1/min, whereas increasing the reaction temperature increased the K_d with 0.0225 1/min at 195 °C. The fastest K_d of 0.0378 1/min is shown at 210 °C.

The K_d value was compared to the delignification constant value reported in the acetic acid treatment for pine wood in the literature section (Vázquez, Antorrena et al. 1997). At the same temperature, 180 °C, faster K_d is observed for the acetic acid with 0.017 1/min over 0.0038 1/min for GVL. It is worth to mention that in most studies, the delignification model adopted a consecutive model, where the rate constant for condensation reactions was also estimated, thus the value of the delignification constant from the consecutive model is not accurate for direct comparison with the single step delignification constant estimated in this study for GVL. The faster K_d values can lead to the hypothesis that acetic acid possesses better solvent properties for lignin over GVL. Furthermore, the K_d values reported were compared to the delignification kinetics reported by (Borrega, Nieminen et al. 2011), also adopting a consecutive model. At 180 °C, using pure water with birch wood, the delignification rate constant was 0.105 1/min, which is significantly higher when compared to the 0.0038 1/min for GVL. Also at 200 °C, the delignification rate constant of birch was more than 10-fold faster than at 195 °C. The faster rates in delignification can be explained by the nature of lignin in hardwood and softwood. Softwood lignin is known to have higher resistance to delignification.

The activation energy required to initiate the delignification reactions was obtained from

Arrhenius equation.

$$K_d = Ae^{Ea/RT}$$

Where, Kd is the delignification rate constant in 1/min.

A is the Arrhenius constant that explains the proper collision and fraction between particles necessary to initiate the reaction.

Ea is the activation energy in J/mol.

R is the universal gas constant in J/mol.K

T is the temperature of the reactions in K.

Measuring the value of the activation energy is done by plotting the natural logarithms (Ln) of K equivalent to each reaction temperature against the inverse of T. The deduced equation then follows a straight line equation, with intercept of 1/A and slope of Ea/R (shown in Fig. 39 below). The activation energy was found to be 140.1 KJ/mol. The diversion of the three points below from a straight line can be explained by the difference in particle size used in the 210 °C series.

$$Ln\ K_d = \frac{Ea}{R}\frac{1}{T} + Ln\ A$$

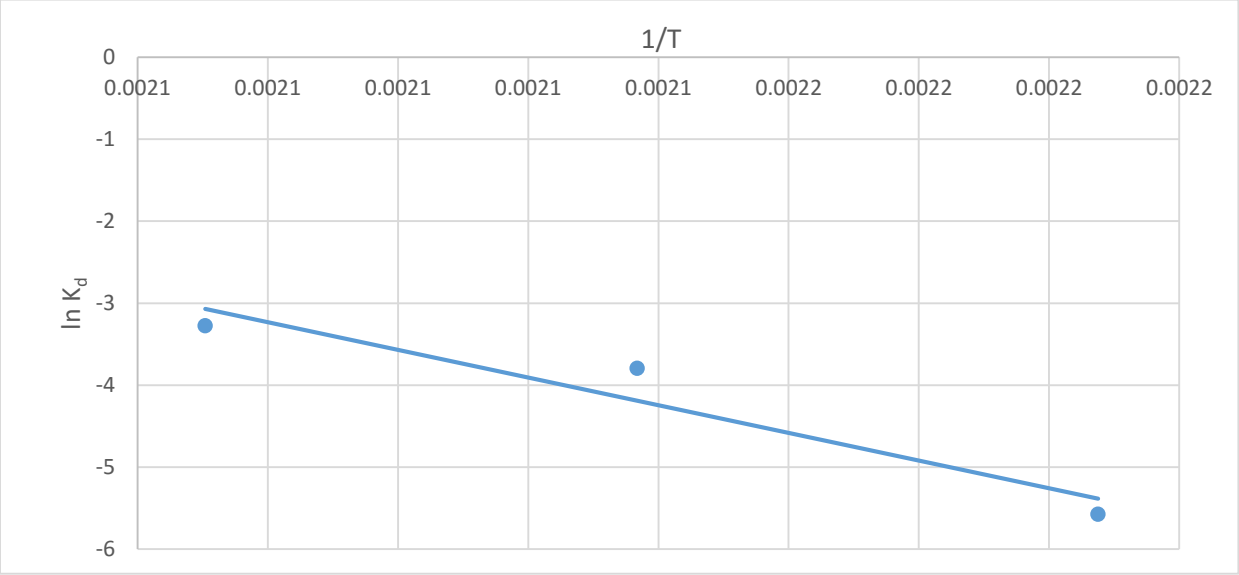


Fig. 39 *Activation energy required for delignification*

Similar to the model built for delignification, a similar model for the polysaccharides degradation in pulp could be deduced. The rate constants were obtained from fitting a curve model to the GGM

and xylan data points separately. These fittings were also done aided by the non-linear functions in Wolfram Mathematica 10.3.

The models were also assumed to follow first order reaction orders for simplification. The curves fitting can be observed in the Fig. 40, Fig. 41 and Fig. 42 below. At 180 °C, cellulose degradation is slower than at 210 °C with 0.0006 compared to 0.0054 1/min (Table 16). Hemicelluloses hydrolysis were, on the other hand, much faster than that of cellulose due to their amorphous structure. This is demonstrated in the energy required to initiate the hydrolysis reactions for hemicelluloses, 90.3 KJ/mol for GGM and 84.1 KJ/mol for xylan, which is less than the energy required for cellulose hydrolysis with 134.2 KJ/mol.

In (Parajo, Alonso et al. 1995), the use of HCl catalyst with 95% acetic acid yield faster degradation rates for cellulose over the data reported here. The effect of the catalyst, 0.15% concentration, can be noticed even at a lower temperature of 130 °C, in which faster cellulose degradation with 0.001 1/min is observed. On the other hand, hemicellulose degradation was almost the same as reported here with combined, xylan and GGM, hydrolysis rate of 0.29 1/min.

Table 16 Activation energies and rate constants for cellulose, GGM and xylan at 180, 195 and 210 °C

Temp, °C	**180**	**195**	**210**	**Ea KJ/mol**	
K_c, 1/min	0.0006	0.0039	0.0054	**Cellulose**	134.2
K_{GGM}, 1/min	0.0102	0.0342	0.0448	**GGM**	90.3
K_{Xyl}, 1/min	0.0222	0.0622	0.0882	**Xylan**	84.1

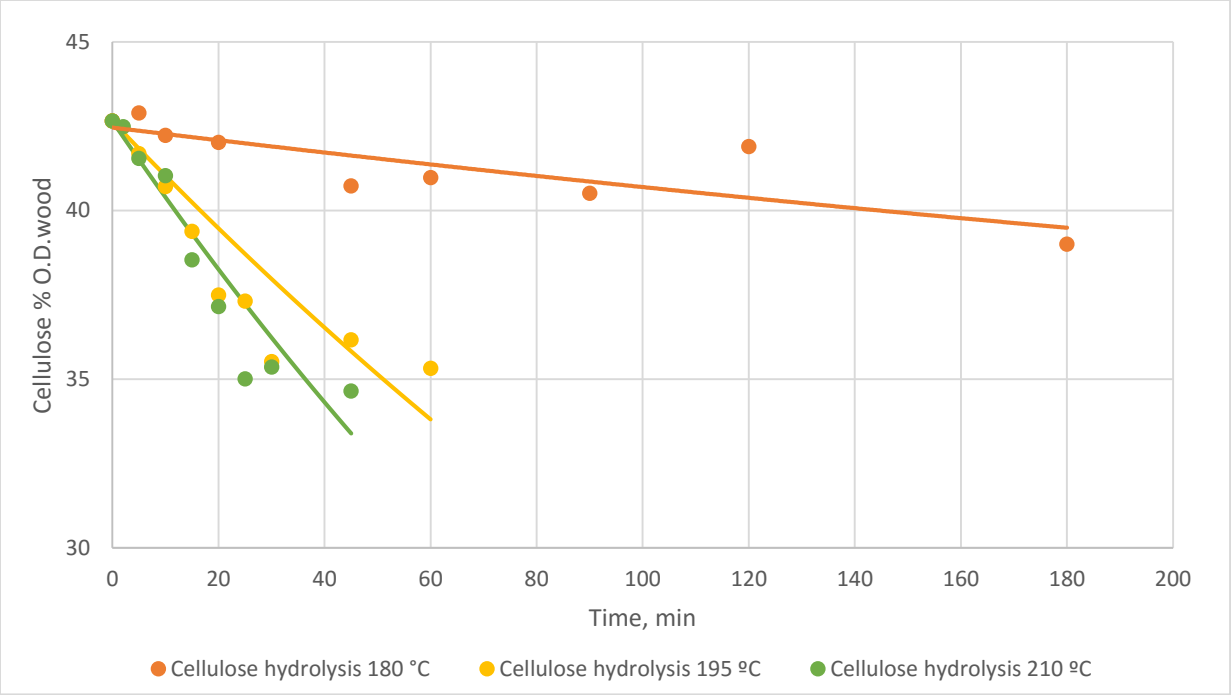


Fig. 40 *Model of cellulose hydrolysis yield loss at 180, 195 and 210 °C*

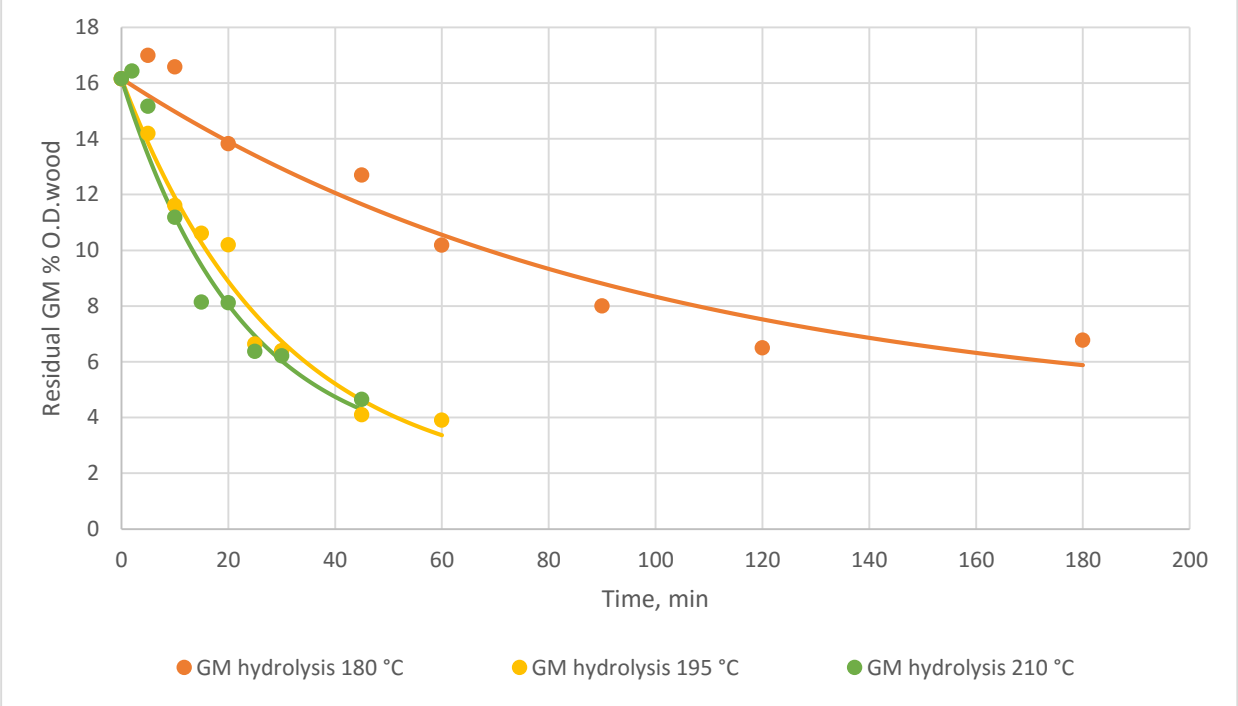


Fig. 41 *Model of GM hydrolysis at 180, 195 and 210 °C*

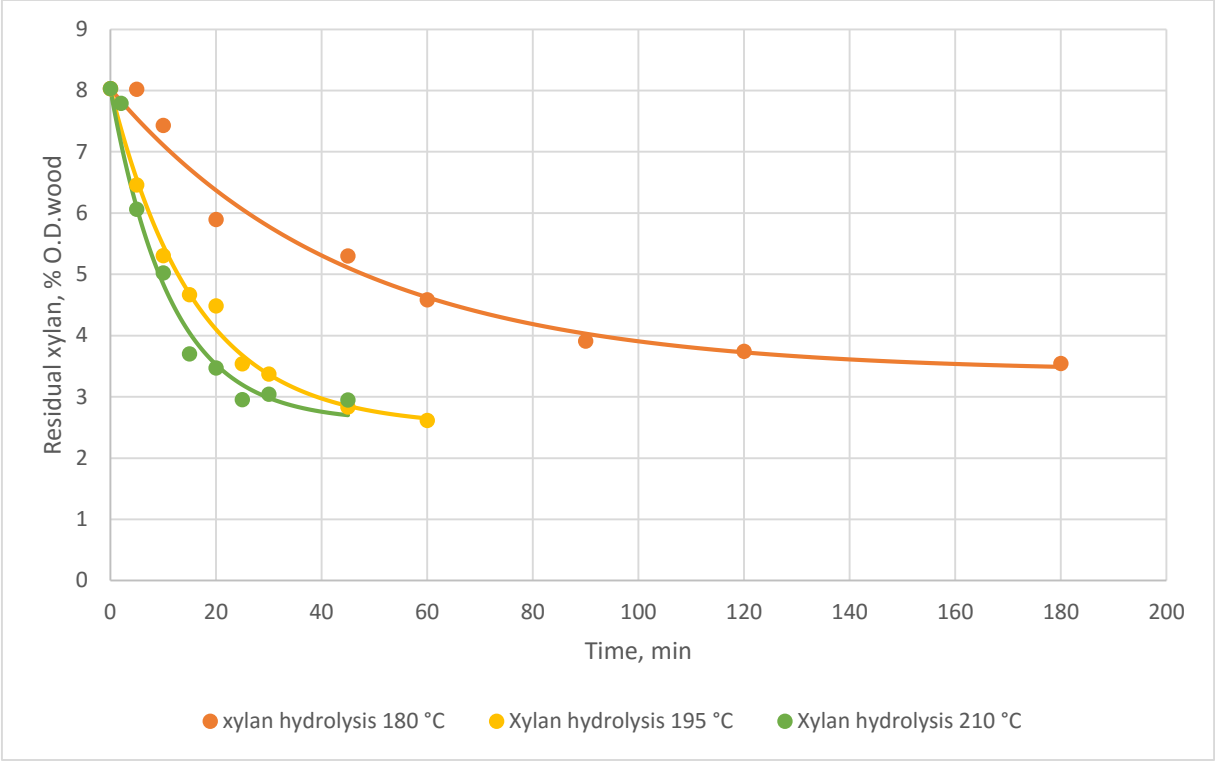


Fig. 42 *Model of xylan hydrolysis at 180, 195 and 210 ℃*

A selectivity term could then be defined for the above reaction, defined as the rate of delignification in pulp compared to the rate of cellulose degradation.

$$Selectivity = \frac{K_d(\ delignification\ rate\ constant)}{K_C\ (cellulose\ yield\ loss\ rate)}$$

The derived values of selectivity show that the change in the delignification rate to the cellulose loss rate over certain range of temperature is almost the same, with 6.85 at 180 °C, 5.81 at 195 °C and 6.95 at 210 °C. The increase in temperature increase the delignification rate as seen above but on the other hand, the cellulose losses also increase. Thus, the selectivity remains almost unaffected.

5. Observations and recommendations

The correlation between the rapid increase in the reaction temperature and the particle size of the pine was observed during the experiments. The monowave reactor uses 850 W power to heat up the reaction mixture to the required temperature in a time interval of 1.5 to 2 minutes. This fast increase in temperature in a short period of time with the used particle size 0.125 mm showed a big leap in the system pressure during the heating up period. This leap was significantly noticed in the 210 °C series, where the system pressure exceeded 32 bars (system pressure limitation) from 17 bar at 195 °C and 14 bar at 180 °C. Hence, forced the reactor to lower the heating energy to decrease the pressure back. It's worth to notice that this sudden change in the system power and consequently pressure affected the products of the reaction. This problem only showed in the 210 °C, as for the 180 °C and 195 °C there was no overshooting in the system pressure. To overcome this problem, two alternative methods were suggested. One was to eliminate the fast heating up time with setting a fixed heating up time interval for the reactor, the heating up interval was chosen to be 15 min then the reaction temperature was hold constant for a calculated time before cooling down the mixture. The reaction heating up interval with the holding time were deduced from the equivalent isothermal heating time for the reaction. The approach was a rough assumption since the hydrolysis and degradation reactions commence while heating up and during the hold-up time. The other alternative is to use a larger particle size for the 210 °C series. Milled pine of 0.2-0.225 mm particle size was tested for rapid heating. The results showed no overshooting in pressure with the system overall pressure maintained between 21-24 bar. This also suggests that the increase in pressure was the result of degradation and evaporation of highly volatile extractive compounds (mainly terpenes) especially that they are easily accessible in extremely small particle size. The yield and delignification values for this series showed no notable difference than the delignification carried out using the 0.125 mm particle size at the same temperature, 210 °C. In addition, the yield values for the 0.2-0.225 mm at 210 °C were less than the corresponding ones at 195 °C for 0.125 mm, with 50% yield after 30 mins at 210 °C using the 0.2-0.225 mm particle size and 60% yield after 30 mins at 195 °C using 0.125 mm particle size. Thus, the latter alternative was chosen and the series was carried out for the 210 °C. The pressure, time vs power profiles of the experiments where the problem was noticed as well as when a higher particle size is used are shown in Appendix 3: monowave overshooting graphs.

6. Conclusion

GVL in this report was proposed as an organosolv treatment in the fractionation of milled pine wood. The use of the solvent would hydrolyze the wood into its main constituents, thus, achieving the biorefinery concept. Moreover, the use of GVL as a solvent fulfills the green biorefinery concept, since GVL is a sustainable solvent that can be produced from the products fractionation

process by further hydrogenation of levulinic acid. The separation and recycling of GVL from the process is simple and can be achieved by a distillation process, since there is no azeotrope formation with water and its low vapor pressure.

Agreeing with the reports mentioned in the literature review section, the results presented hereby confirm that GVL improves the hydrolysis reactions of pine wood over using pure water. Residual lignin of 14.2% O.D. wood is observed after 180 minutes of reaction time at 180 °C, although only 5.6% O.D. wood of residual lignin remains after 45 minutes at 210 °C. However, the lignin value is still considerably high when compared to that produced from the delignification of eucalyptus and birch wood under the same or similar reaction conditions. Hence, treatments at higher temperature can be proposed or the use of small amount of acid catalyst. The use of acid catalyst (H_2SO_4) is expected to significantly reduce the residual lignin amount, making better utilization of the produced fibers. But on the other hand the use of H_2SO_4 will contradict the concept of producing sulfur-free pulp, which is one of the main advantages of the GVL solvent. Other organosolvents such as acetic acid showed better delignification figures (Vázquez, Antorrena et al. 1997), over the figures reported here when no catalyst was used. In general, most of the organosolv treatments use small amount of H_2SO_4 to achieve satisfactory delignification.

Delignification kinetics showed increase in the rate constants, faster delignification, at higher temperatures 195 °C and 210 °C than at 180 °C. Even though the loss in polysaccharides especially cellulose also increase at higher temperature, but the delignification selectivity is not affected. Polysaccharides kinetics also showed faster hydrolysis in a temperature dependent behavior, with increase in the hydrolysis reactions, especially of hemicelluloses due to their amorphous structure that is easily hydrolyzed. Cellulose too showed higher losses when temperature was raised to some extent. The low amounts of the degradation reactions, acids and furfurals, can be explained by the absence of acid catalysts and the GVL/H_2O ratio (Luterbacher, Rand et al. 2014). While the role of GVL in limiting these reactions is not yet confirmed. Furfurals yield was of less than 1% and the detected amounts of levulinic acid and formic acid were around 2%. Acetic acid was minor and in some points not detected in the analysis.

7. References

ALONSO, D.M., WETTSTEIN, S.G. and DUMESIC, J.A., 2013. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. *Green Chemistry*, **15**(3), pp. 584-595.

BLECHSCHMIDT, J. and HEINEMANN, S., 2008. Introduction. *Handbook of Pulp*. Wiley-VCH Verlag GmbH, pp. 1069-1072.

BORREGA, M., NIEMINEN, K. and SIXTA, H., 2011. Effects of hot water extraction in a batch reactor on the delignification of birch wood. *BioResources,* **6**(2), pp. 1890-1903.

BRITT, K.W., 1964. Handbook of pulp and paper technology. *Handbook of pulp and paper technology.* Reinhold Publishing Corp., .

BROEKHUIS, A.A., HEERES, H.J. and CHALID, M., 2012. Green Polymer Precursors from Biomass-Based Levulinic Acid. *Procedia Chemistry,* **4**(1), pp. 260-267.

CHUNDAWAT, S.P., BECKHAM, G.T., HIMMEL, M.E. and DALE, B.E., 2011. Deconstruction of lignocellulosic biomass to fuels and chemicals. *Annual review of chemical and biomolecular engineering,* **2**, pp. 121-145.

CLAIR, B., ALMÉRAS, T., YAMAMOTO, H., OKUYAMA, T. and SUGIYAMA, J., 2006. Mechanical Behavior of Cellulose Microfibrils in Tension Wood, in Relation with Maturation Stress Generation. *Biophysical journal,* **91**(3), pp. 1128-1135.

FANG, W., SIXTA, H., 2015. Advanced Biorefinery based on the Fractionation of Biomass in g-Valerolactone and Water. *ChemSusChem*, **8**(1), pp.73-76.

FENGEL, D. and WEGENER, G., 1983. *Wood: chemistry, ultrastructure, reactions.* Walter de Gruyter.

GIERER, J., 1986. Chemistry of delignification. *Wood Science and Technology,* **20**(1), pp. 1-33.

GIRISUTA, B., 2007. *Levulinic acid from lignocellulosic biomass*, [University Library Groningen].

GORDOBIL, O., MORIANA, R., ZHANG, L., LABIDI, J. and SEVASTYANOVA, O., 2016. Assesment of technical lignins for uses in biofuels and biomaterials: Structure-related properties, proximate analysis and chemical modification. *Industrial Crops and Products,* **83**, pp. 155-165.

HAMELINCK, C.N., VAN HOOIJDONK, G. and FAAIJ, A.P., 2005. Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle-and long-term. *Biomass and Bioenergy,* **28**(4), pp. 384-410.

HON, D.N. and SHIRAISHI, N., 2000. *Wood and cellulosic chemistry, revised, and expanded.* CRC Press.

HORVÁTH, I.T., MEHDI, H., FÁBOS, V., BODA, L. and MIKA, L.T., 2008. γ-Valerolactone—a sustainable liquid for energy and carbon-based chemicals. *Green Chemistry,* **10**(2), pp. 238-242.

HORVTH, I.T., 2008. Solvents from nature. *Green Chemistry,* **10**(10), pp. 1024-1028.

IAKOVLEV, M., YOU, X., VAN HEININGEN, A. and SIXTA, H., 2014. SO2–ethanol–water (SEW) fractionation process: production of dissolving pulp from spruce. *Cellulose,* **21**(3), pp. 1419-1429.

JANSON, J., 1970. Calculation of the polysaccharide composition of wood and pulp. *Paperi ja Puu,* **52**(5), pp. 323-329.

JOHANSSON, A., AALTONEN, O. and YLINEN, P., 1987. Organosolv pulping—methods and pulp properties. *Biomass,* **13**(1), pp. 45-65.

KAMIDE, K., 2005. 1 - Introduction. In: K. KAMIDE, ed, *Cellulose and Cellulose Derivatives.* Amsterdam: Elsevier, pp. 1-23.

Le, Q., MA, Y., BORREGA, M. and SIXTA, H., unpublished, submitted 2016. Wood biorefinery based on γ-valerolactone/water fractionation.

LI, W., XIE, J., LIN, H. and ZHOU, Q., 2012. Highly efficient hydrogenation of biomass-derived levulinic acid to γ-valerolactone catalyzed by iridium pincer complexes. *Green Chemistry,* **14**(9), pp. 2388-2390.

LUTERBACHER, J.S., AZARPIRA, A., MOTAGAMWALA, A.H., LU, F., RALPH, J. and DUMESIC, J.A., 2015. Lignin monomer production integrated into the γ-valerolactone sugar platform. *Energy Environ. Sci, **8***(9), pp.2657-2663.

LUTERBACHER, J.S., RAND, J.M., ALONSO, D.M., HAN, J., YOUNGQUIST, J.T., MARAVELIAS, C.T., PFELGER, B.F. and DUMESIC, J.A., 2014. Nonenzymatic sugar production from biomass using biomass-derived γ-valerolactone. *Science, **343***(6168), pp.277-280.

LUTHE, C.E., 1990. Isolation and characterization of lignosulphonates from an ultra high yield neutral sulphite pulping effluent. *Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood,* **44**(2), pp. 107-112.

MARTINALONSO, D. and MARCEL R GALLO, J., 2013. Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. *Catalysis Science & Technology,* **3**(4), pp. 927-931.

MCDONOUGH, T.J., 1992. The chemistry of organosolv delignification. *Tappi J,* **76**(8), pp. 186-193.

MELLMER, M.A., ALONSO, D.M., LUTERBACHER, J.S., GALLO, J.M.R. and DUMESIC, J.A., 2014. Effects of γ-valerolactone in hydrolysis of lignocellulosic biomass to monosaccharides. *Green Chemistry,* **16**(11), pp. 4659-4662.

MORAIS, A.R. and BOGEL-LUKASIK, R., 2013. Green chemistry and the biorefinery concept. *Sustainable Chemical Processes,* **1**(1), pp. 18.

MUÑOZ, C., MENDONÇA, R., BAEZA, J., BERLIN, A., SADDLER, J. and FREER, J., 2007. Bioethanol production from bio-organosolv pulps of Pinus radiata and Acacia dealbata. *Journal of Chemical Technology and Biotechnology,* **82**(8), pp. 767-774.

PARAJO, J.C., ALONSO, J.L. and SANTOS, V., 1995. Kinetics of Catalyzed Organosolv Processing of Pine Wood. *Industrial & Engineering Chemistry Research,* **34**(12), pp. 4333-4342.

SANNIGRAHI, P., MILLER, S.J. and RAGAUSKAS, A.J., 2010. Effects of organosolv pretreatment and enzymatic hydrolysis on cellulose structure and crystallinity in Loblolly pine. *Carbohydrate research,* **345**(7), pp. 965-970.

SANNIGRAHI, P. and RAGAUSKAS, A.J., 2013. Fundamentals of Biomass Pretreatment by Fractionation. *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals.* John Wiley & Sons, Ltd, pp. 201-222.

SCHOLS, H.A., GARROTE, G., FALQUE, E., DOMINGUES, H., KABEL, M.A. and PARAJO, J.C., 2007. Effects of Eucalyptus globulus Wood Autohydrolysis Conditions on the Reaction Products. *Journal of Agricultural and Food Chemistry,* **55**(22), pp. 9006-9013.

SHELDON, R.A., 2014. Green and sustainable manufacture of chemicals from biomass: state of the art. **16**(3), pp. 95-963.

SIXTA, H., 2006. Introduction. *Handbook of Pulp.* Wiley-VCH Verlag GmbH, pp. 2-19.

SIXTA, H., POTTHAST, A. and KROTSCHEK, A.W., 2008. Chemical Pulping Processe: Sections 4.1-4.2.5. *Handbook of Pulp.* Wiley-VCH Verlag GmbH, pp. 109-229.

SJÖSTRÖM, E., 1993a. Chapter 1 - THE STRUCTURE OF WOOD. In: E. SJÖSTRÖM, ed, *Wood Chemistry (Second Edition).* San Diego: Academic Press, pp. 1-20.

SJÖSTRÖM, E., 1993b. Chapter 2 - INTRODUCTION TO CARBOHYDRATE CHEMISTRY. In: E. SJÖSTRÖM, ed, *Wood Chemistry (Second Edition).* San Diego: Academic Press, pp. 21-50.

SJÖSTRÖM, E., 1993c. Chapter 3 - WOOD POLYSACCHARIDES. In: E. SJÖSTRÖM, ed, *Wood Chemistry (Second Edition).* San Diego: Academic Press, pp. 51-70.

SJÖSTRÖM, E., 1993d. Chapter 4 - LIGNIN. In: E. SJÖSTRÖM, ed, *Wood Chemistry (Second Edition).* San Diego: Academic Press, pp. 71-89.

SJÖSTRÖM, E., 1993e. Chapter 7 - WOOD PULPING. In: E. SJÖSTRÖM, ed, *Wood Chemistry (Second Edition).* San Diego: Academic Press, pp. 114-164.

TANBDA, H., NAKANO, J., HOSOYA, S. and CHANG, H.M., 1987. Stability of α-ether type model compounds during chemical pulping processes. *Journal of Wood Chemistry and Technology,* **7**(4), pp. 485-497.

TANG, X., ZENG, X., LI, Z., HU, L., SUN, Y., LIU, S., LEI, T. and LIN, L., 2014. Production of γ-valerolactone from lignocellulosic biomass for sustainable fuels and chemicals supply. *Renewable and Sustainable Energy Reviews,* **40**, pp. 608-620.

VÁZQUEZ, G., ANTORRENA, G., GONZÁLEZ, J., FREIRE, S. and LÓPEZ, S., 1997. Acetosolv pulping of pine wood. Kinetic modelling of lignin solubilization and condensation. *Bioresource Technology,* **59**(2), pp. 121-127.

WU, M., LIU, J., YAN, Z., WANG, B., ZHANG, X., XU, F. and SUN, R., 2016. Efficient recovery and structural characterization of lignin from cotton stalk based on a biorefinery process using a γ-valerolactone/water system. *RSC Advances,* **6**(8), pp. 6196-6204.

YAN, K., YANG, Y., CHAI, J. and LU, Y., 2015. Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals. *Applied Catalysis B: Environmental,* **179**, pp. 292-304.

8. Appendices

Appendix 1: Polysaccharides and lignin estimation, Janson formulas

The values of monosaccharides, acids and furfurals detected were traced back to the primary polysaccharides based on oven dry wood basis. First, in pulp, using Janson formulas (Janson 1970), arabinose, xylose, glucose, mannose and galactose could be traced back to their polysaccharides.

Full chemical pine sulphite pulp was chosen as a model from Janson formulas. The choice of the model was based on the same wood specimen and acidic cooking conditions. Janson constants, U = 11 and M = 3.3, where U is the uronic acid % in xylan and M is the molar ratio of mannose to glucose in glucomannan (Janson 1970).

The formulas described in Appendix 1 to determine the values of the polymers in the pulp are for relatively low yield pulps “Poly 1” (Janson 1970). Auxiliary variables are used in the calculation of the cellulose, xylan and glucomannan. The variables are S, P, AA and N.

S is the amount of lignin and extractives after cooking, since extractives were not determined before or after cooking. Hence, they were assumed to be completely removed during cooking. Thus, S is entirely linin content in pulp after cooking. P is the fraction of other polymers existing in pulp. As for AA, it is the percentage of other molecules found in pinewood xylan. Finally, N is a factor considering the amount of hemicelluloses after cooking (Janson 1970).

Where cellulose, GM and xylan have dimensions of g/g pulp and can be traced back to g/g wood by multiplying by dry matter content.

For non-cooked pinewood. Janson formulas were also used to estimate the original constituents. The model used was “Poly 2” for wood and high yield pulp. The values of the constants U, A, M, G and V, as well as the auxiliary variables and the polysaccharides formulas can be found in the reference (Janson 1970).

Pulp consisted of the residual fibers, cellulose and hemicelluloses, in addition to the residual lignin. For spent liquor. Glucose was traced back to glucan. Whereas, values of arabinan, galactan, mannan, rhamnan and xylan, were all calculcated from their forming monosaccharides, arabinose, galactose, mannose, rhamnose and xylose respectively. Lignin value from UV-spectrophotometry is also shown below.

The overall values of the main polysaccharides (cellulose, GGM and xylan) and lignin were estimated by adding the values of the constituents found in pulp, spent and washing liquors. First, cellulose consisted of cellulose in pulp and fraction of glucan in spent liquor. On the other side, HMF, acetic acid, formic acid, levulinic acid, galactan and mannan in liquor, along with GGM in pulp formed the overall amount of GGM. Furfural in spent liquor along with the amount of xylan calculated in spent liquor and pulp formed the overall xylan amount. Finally, the overall value of lignin is the sum of ASL and Klason lignin in pulp, lignin in SL and washing liquor lignin.

$$S = extractives\ + lignin$$

$$P = 1 - \frac{S}{100}$$

$$AA = 100 - U$$

$$N = 88\frac{arabinose\ + xylan}{AA} + 0{,}9\ (galactose + glucose + mannose)$$

$$Cellulose = \frac{90\ (glucose * M - mannose)P}{N * M}$$

$$GM = \frac{90\ (galactose * M + mannose * M + mannose)P}{N * M}$$

$$Xylan = \frac{8800\ (arabinose + xylan)P}{N * AA}$$

Appendix 2: Components mass balance

Table 17 Components mass balance for the GVL-H2O series at 180 °C and 120 min

	%GVL	0	10	20	35	50	60	75	98	50H	60H	50L	60L
% O.D.wood	**Pulp**												
	Xylan	2	2	2.2	2.6	3.5	4.1	5	8.6	1.6	2.6	2.6	4
	GGM	2	1.7	1.9	2.6	4.5	6.8	11.3	16.6	1	2.8	2.5	6.6
	Cellulose	39.3	38.5	39.5	39	39.5	39.6	39.7	44.2	36.7	37.6	36.9	39
	Lignin	27.5	23.4	20.5	15.5	12.7	14.4	15.8	20.7	7.5	5.9	10	14.7
	Yield	71	66	64	60	60	65	72	90	47	49	52	64
	SL												
	Mono/Total sugars, %	47.1	47.2	43.7	44	24.7	24.9	31.7	0	54.6	36.8	42.2	21.8
	Glucan	2.9	3.1	2.9	2.4	2.2	1.3	0.3	0	1.9	1.8	2.2	1.4
	Xylan	2.2	2.1	2.1	1.8	2	1.2	0.3	0	0.3	0.4	1	1.3
	Mannan	7.4	7.5	7.6	6.5	6.1	3.6	0.7	0	2.5	3.2	5	3.8
	Galactan + Arab+ Rham	2	2.1	2	1.8	2.1	1.5	0.6	0	0.4	0.5	1.2	1.6
	Lignin	0.7	1.5	2.6	4.9	8.9	9.9	11	5.3	13.4	13	11.1	10.7
	Total	15.2	16.3	17.3	17.4	21.3	17.5	12.9	5.3	18.4	18.9	20.3	18.8
	Acids and furfurals												
	Formic acid	1.14	1.39	1.35	1.93	1.99	1.92	1.13	0.82	0.64	0.7	1.93	1.35
	Acetic acid	0.87	0.76	0.6	0.59	0.34	0.05	0.21	0	2.07	1.65	0.98	0.28
	Levulinic acid	2.63	1.61	2.08	2.48	2.63	3.15	2.71	0	2.59	1.44	2.52	1.67
	HMF	0.42	0.71	0.39	0.31	0.08	0.04	0.03	0	1.5	0.54	0.48	0.03
	Furfural	0.8	0.9	0.8	0.8	0.3	0.2	0.1	0	1.3	0.6	1	0.1
	Washing water lignin												
	EtOH lignin	0.06	3.3	3.7	4	2.5	2	3.5	1.6	3.3	2.8	2.6	2.4

Table 18 Components mass balance for the time series at 180 °C

180 °C	Time, min	5	10	20	45	60	90	120	180
% O.D.wood	**Pulp**								
	Xylan	8	7.4	5.9	5.3	4.6	3.9	3.7	3.5

	GGM	17	16.6	13.8	12.7	10.2	8	6.5	6.8
	Cellulose	42.9	42.2	42	40.7	41	40.5	41.9	39
	Lignin	25.3	24.9	22.4	21.7	19.2	17.1	15	14.2
	Total	93	91	84	80	75	70	67	64
	SL								
	Mono/Total sugars, %	42.30	51.20	29.80	26.80	21.00	22.10%	24.40%	28.10%
	Glucan	0.1	0.1	0.4	0.4	1	1.2	1.5	1.6
	Xylan	0.1	0.2	0.7	0.8	1.4	1.3	1.4	1.1
	Mannan	0.3	0.3	1.4	1.4	3.2	3.7	4.5	4.6
	Galactan + Arab+ Rham	0.9	1	1.8	1.7	2	1.6	1.6	1.4
	Lignin	3.9	4.4	5.7	6.8	7.8	9.9	10.6	10.8
	Total	5.3	6.1	10	11.1	15.4	17.8	19.6	19.6
	Acids and furfurals								
	Formic acid	4.19	4.08	3.85	2.88	2.28	1.97	1.97	2.01
	Acetic acid	0	0	0	0	0	0	0	0
	Levulinic acid	0.33	0.34	0.32	0	0	0	0	0
	HMF	0	0	0.01	0.02	0.05	0.11	0.19	0.37
	Furfural	0.01	0.02	0.05	0.09	0.21	0.36	0.54	0.86
	Washing water								
	EtOH lignin	1.08	1.19	1.58	1.62	2.29	2.47	2.55	2.46

Table 19 Components mass balance for the time series at 195 °C

195 ℃	Time, min	5	10	15	20	25	30	45	60
% O.D.wood	**Pulp**								
	Xylan	6.5	5.3	4.7	4.5	3.5	3.4	2.8	2.6
	GGM	14.2	11.6	10.6	10.2	6.6	6.4	4.1	3.9
	Cellulose	41.7	40.7	39.4	37.5	37.3	35.5	36.2	35.3
	Lignin	23.1	20.7	18.3	17.8	14.2	12.2	7.6	8.2
	Total	85	78	73	70	62	57	51	50
	SL								

	Mono/Total sugars, %	36.50	17.40	22.00	19.50	20.40	23.70%	29.00%	35.50%
	Glucan	0.1	0.5	0.8	0.8	1.3	1.2	1.7	1.5
	Xylan	0.1	0.8	1	1	1.3	1.3	0.8	0.8
	Mannan	0.4	1.9	2.5	2.5	3.8	3.5	4.1	3.8
	Galactan + Arab+ Rham	1	1.6	1.6	1.7	1.3	1.4	0.8	0.8
	Lignin	3.3	6.4	6.4	7.8	9.6	12	12.4	13.3
	Total	5	11.2	12.3	13.7	17.5	19.3	19.9	20.3
	Acids and furfurals								
	Formic acid	3.16	3.67	2.98	2.3	2.22	2.35	1.65	1.51
	Acetic acid	0	0	0	0	0	0	0	0
	Levulinic acid	2.42	2.54	1.48	1.22	0.79	1.01	0.98	0.54
	HMF	0	0.01	0.02	0.03	0.11	0.18	0.4	0.44
	Furfural	0	0.08	0.09	0.1	0.31	0.34	0.69	0.72
	Washing water								
	EtOH lignin	1.53	1.89	1.82	2	2.48	2.62	2.67	2.66

Table 20 Components mass balance for the time series at 210 °C

210 °C	**Time, min**	**2**	**5**	**10**	**15**	**20**	**25**	**30**	**45**
% O.D.wood	**Pulp**								
	Xylan	7.8	6.1	5	3.7	3.5	3	3	2.9
	GGM	16.4	15.2	11.2	8.1	8.1	6.4	6.2	4.7
	Cellulose	42.5	41.5	41	38.5	37.2	35	35.4	34.7
	Lignin	24.4	22.1	20	16.7	13	11.3	6.9	5.6
	Total	91	85	77	67	62	56	52	48
	SL								

	Mono/Total sugars, %	26.30	19.20	20.90	16.30	19.40	17.70%	18.70%	20.00%
	Glucan	0.2	0.7	1.2	1.3	1.3	1.3	1.5	1.5
	Xylan	0.3	0.8	1.2	1.7	1.2	1.3	1.4	1.3
	Mannan	0.8	2.4	3.9	5.2	3.7	4.3	4.5	4.5
	Galactan + Arab+ Rham	1	1.7	1.5	2.1	1.6	1.7	1.4	1.4
	Lignin	4.8	6.4	7.7	8.1	11.1	12.6	14.3	16.2
	Total	7.1	12	15.5	18.3	18.9	21.2	23.1	24.8
	Acids and furfurals								
	Formic acid	2.85	2.73	2.58	2.56	2.41	2.61	2.1	1.43
	Acetic acid	0	0	0	0	0	0	0	0
	Levulinic acid	1.63	1.04	0.96	1.13	1.03	1.03	0.68	0.65
	HMF	0	0	0.02	0.05	0.04	0.13	0.26	0.6
	Furfural	0.01	0.02	0.1	0.15	0.14	0.37	0.54	0.88
	Washing water								
	EtOH lignin	1.3	1.88	2.29	2.55	2.52	2.4	2.6	2.56

Appendix 3: Monowave overshooting graphs

Fig. 43 and Fig. 44 show the overshooting at 210 °C and 0.125 mm particle size. Fig. 45 shows the effect when 0.2 mm particle size was used. Fig. 46 and 47 show the profiles at 180 °C and 195 °C.

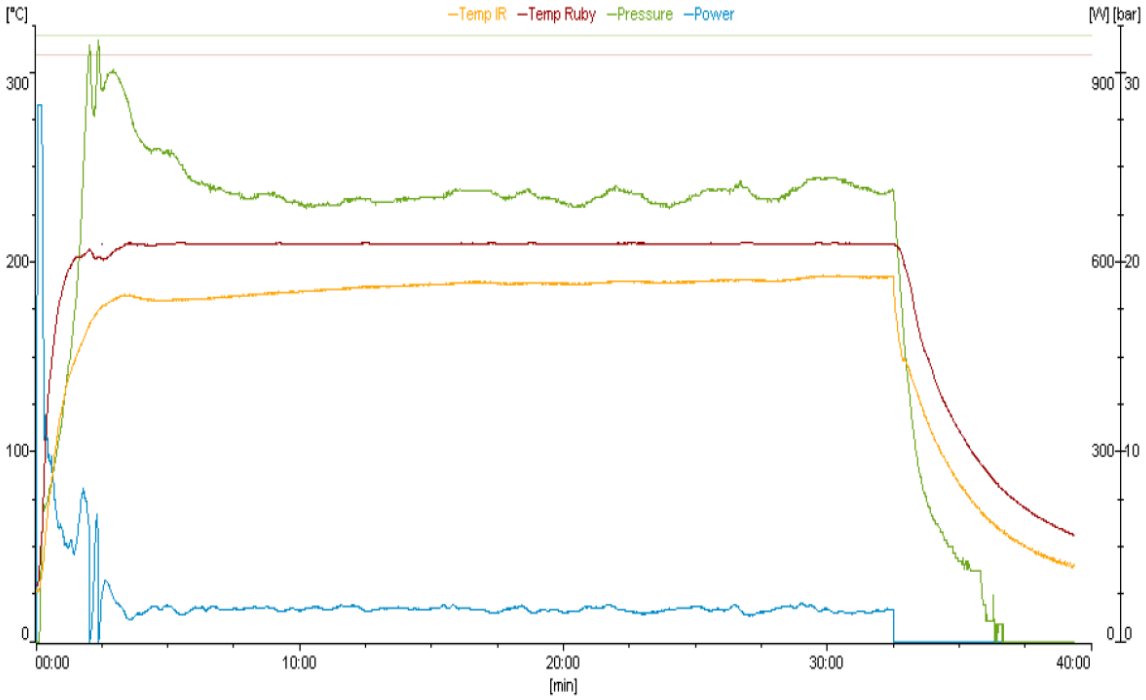


Fig. 43 *Reaction profile at 210 °C with 0.125 mm and 30 min*

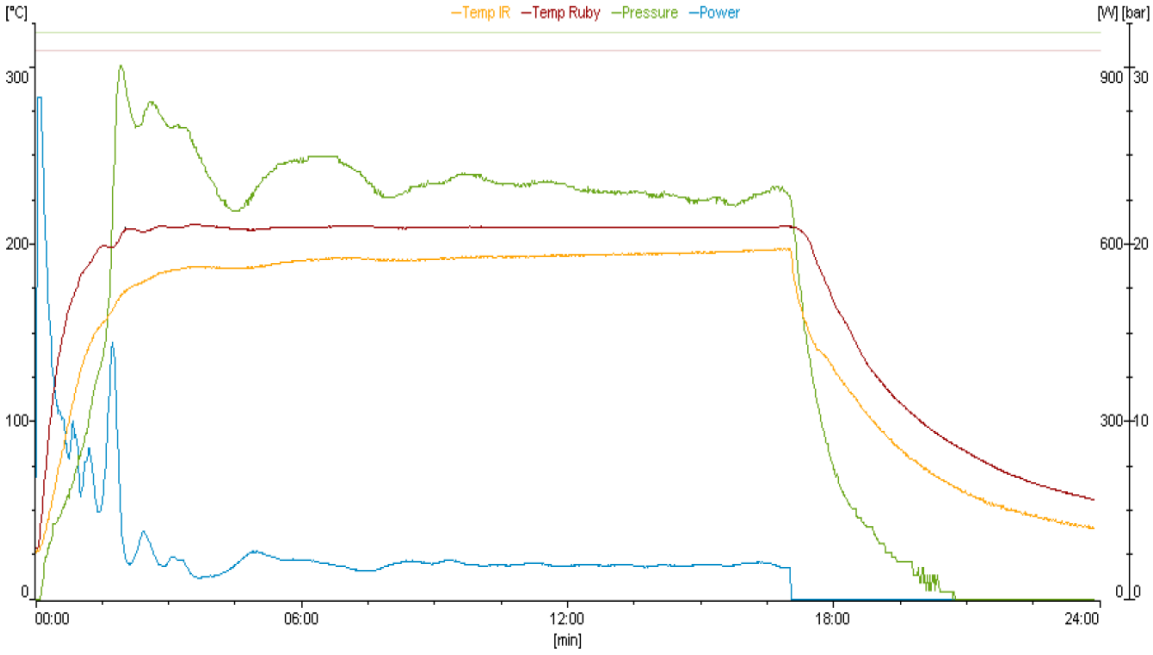


Fig. 44 *Reaction profile at 210 °C with 0.125 mm and 15 min*

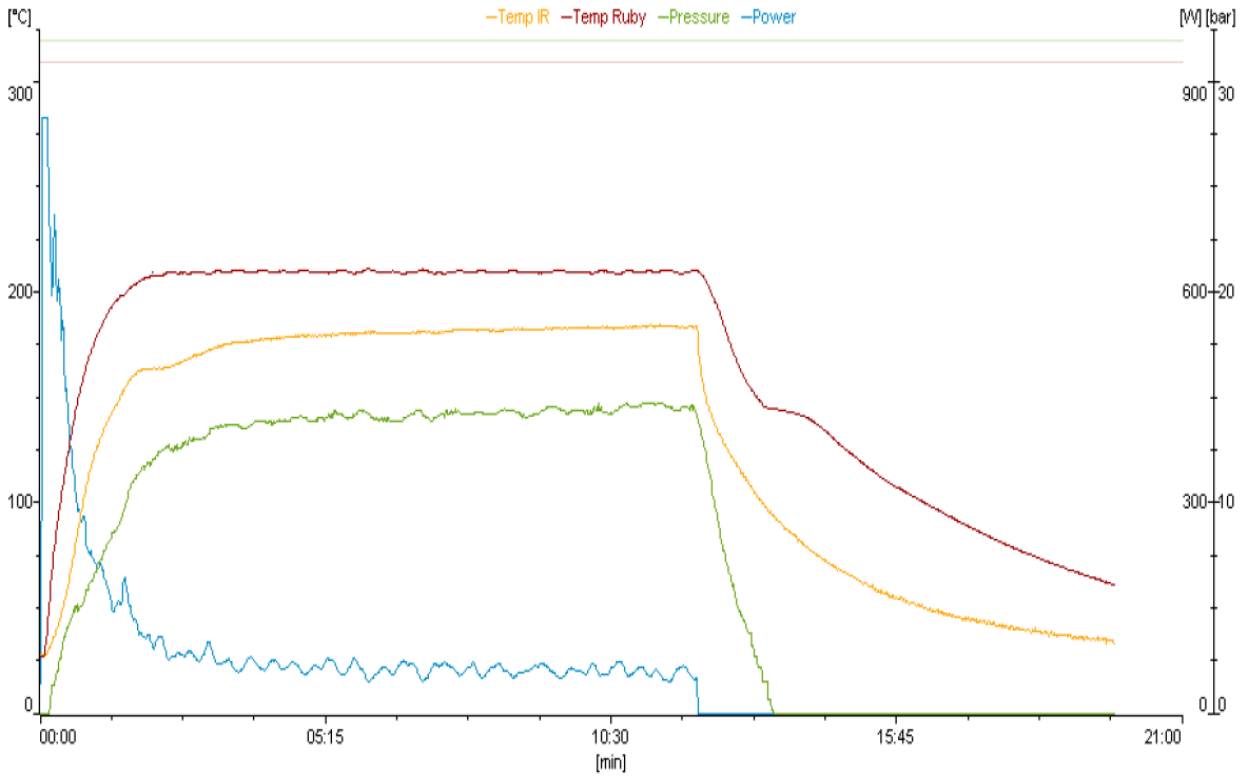


Fig. 45 *Reaction profile at 210 °C with 0.2 mm and 10 min*

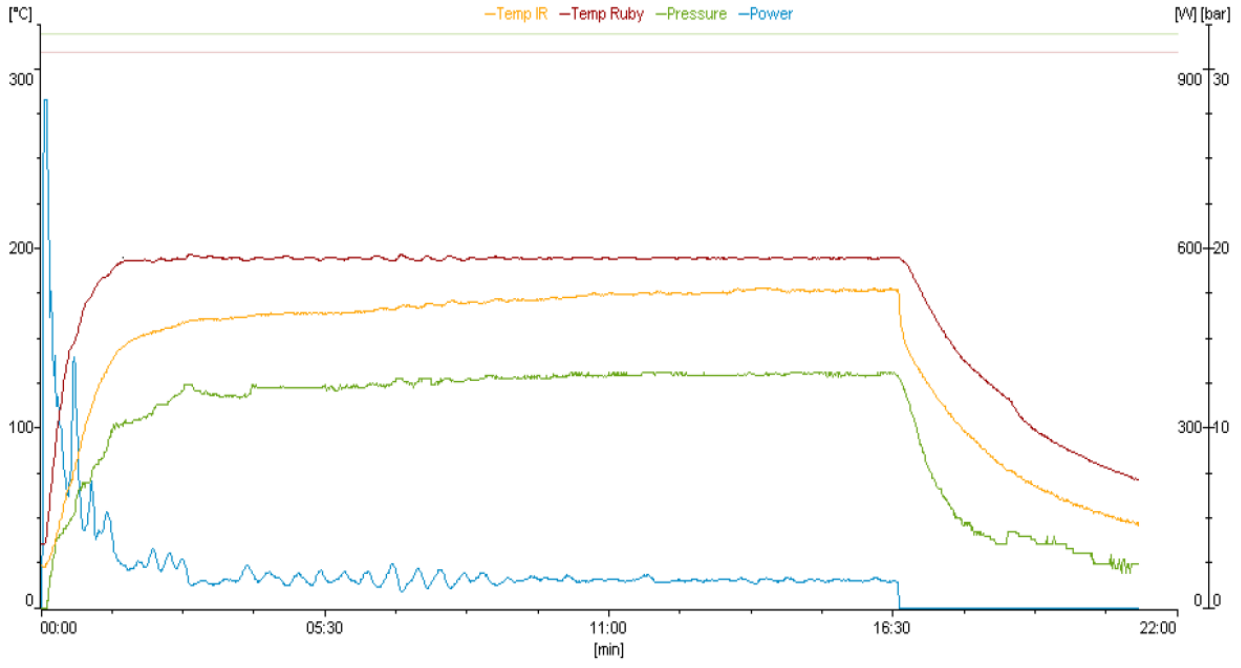


Fig. 46 *Reaction profile at 195 °C with 0.125 mm and 15 min*

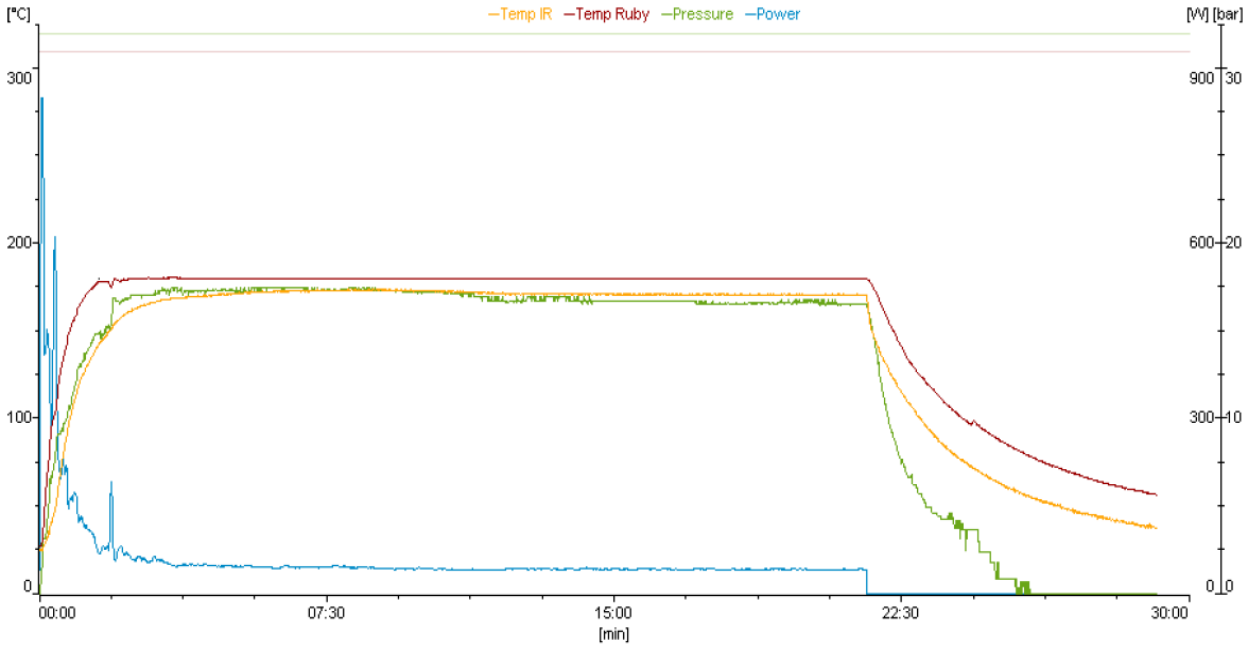


Fig. 47 *Reaction profile at 180 °C with 0.125 mm and 20 min*